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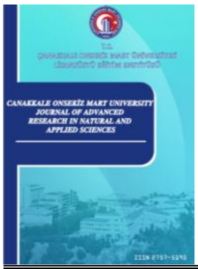

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Azo Dye Removal from Aqueous Solution by Powder Graphite: Investigation of Parameter Effects and Optimization by Box-Behnken Design

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Research Article

Abstract − Industrial wastewaters containing dyes comprise organics that are difficult to biodegrade and when they are discharged to receiving bodies, they cause serious impacts on environment. Therefore, this wastewater requires advanced treatment besides conventional ones. Adsorption is accepted one of the favorable processes, which can be applied integrative to conventional systems during the treatment of this wastewater. In addition to the effectiveness of the materials to be utilized in the adsorption process, their cost and availability are also very important factors. In this study, the efficiency of environmentally friendly, cost-effective powdered graphite was investigated in the removal of diazo type dye (Direct Red 243) from aqueous solution by adsorption. For this purpose, Response Surface Method was applied via Box-Behnken Design and the most effective parameters were investigated in dye adsorption with graphite. Also, the morphology of the graphite before and after adsorption was scanned by Scanning Electron Microscopy. Adsorption study was carried out in batch mode and pH (2-10), adsorbent amount (0.1-1.5 g) and time (15-65 min) were designated as experimental parameters. It has been observed that the most effective parameter in color removal of dye was pH and at low values of this parameters the higher efficiencies were obtained. Additionally, it was observed that the increase in the amount of adsorbent increased the efficiency, and time had no significant effect besides two parameters. Almost complete decolorization (98%) was acquired at pH 2 with 1.5 g adsorbent for 40 min of study. As a result of the study, even it is not improved with further applications, graphite can be effective for anionic dye color removal under acidic conditions by its pristine form.

***Keywords** – Anionic dye, Box-Behnken Design, decolorization, experimental design, graphite adsorption*

1. Introduction

Every year, tons of residual dye containing effluents are produced by textile industries (Choudhary et al., 2020). Especially in third world or some developing countries, the treatment plants to purify these effluents are usually insufficient to meet the discharge standards and they also lack qualified manpower (Khan & Malik, 2014). Besides, in some countries, a tendency to put economic and political concerns before the environment as is often the case, whether the legal regulations are strict or not. So, negative impacts on environment becomes inevitable and feasible solutions are required to compete these impacts. It is important to present easily applicable and cost-effective treatment methods for dye removal. The conventional treatment processes such as biological systems require pre- or post-applications to remove the color and also other pollutants in textile wastewater (Berradi et al., 2019). Among these applications, adsorption shines out as a facile and relatively cost-effective process. Since adsorption accepted as an easy to operate in plant scale, there are several types of adsorbents examined for different textile wastewaters. Especially, dye removal from synthetic aqueous solutions are hugely studied (Ahmad, Eusoff, Oladoye, Adegoke, & Bello, 2020; Lin et al., 2013; Mohebali, Bastani, & Shayesteh, 2019), and these studies are still going on. The adsorbents have great impact on the

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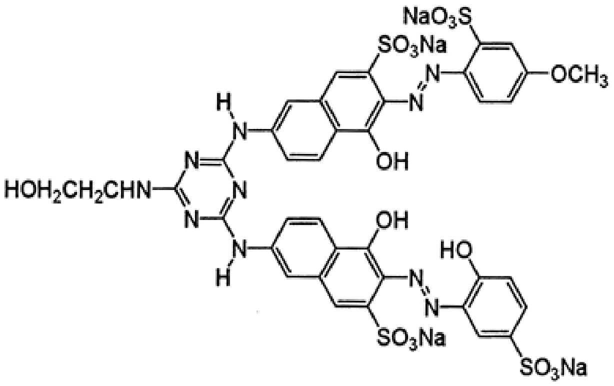
removal efficiencies and the operating expenses of the system (Adeyemo, Adeoye, & Bello, 2017). The alternative adsorbents like charcoal ash (Gengec, Ozdemir, Ozbay, Ozbay, & Veli, 2013), polypyrrole/polyaniline nanofibers (Bhaumik, McCrindle, & Maity, 2013), walnut shell (Dahri, Kooh, & Lim, 2014), pumice (Veliev, Ozturk, Veli, & Fatullayev, 2006), alumina/carbon nanotube hybrid (Malakootian, Mansoorian, Hosseini, & Khanjani, 2015) or struvite (Yetilmezsoy et al., 2020) were investigated for their performance to remove dyes from aqueous solutions. But these materials are usually need further treatment like activation, high temperature carbonization, metal doping etc. and these applications cause increasing costs during production. Pristine graphite is an alternative for its availability and low-cost for adsorption of dyes from aqueous solutions. In literature, there are very little studies for investigating the adsorptive effectiveness of pristine form of graphite, which is free from any further improvement. Usually, the studies focus on surface-enhanced graphites or its composites (Carvallho et al., 2016; Peng, Li, Liu, & Song, 2016; Travlou, Kyzas, Lazaridis, & Deliyanni, 2013).

In this study, powder graphite, which is pristine, was used in the adsorptive removal of anionic dye from aqueous solution and the process was evaluated through Box-Behnken Design to present graphite’s efficiency in dye adsorption. To the best of our knowledge, pristine graphite as an adsorbent for the removal of anionic dye was not investigated through response surface methodology yet. Its effectiveness was examined as an easily accessible and economically rewarding alternative adsorbent.

2. Materials and Methods

Analytical grade chemicals were used during the experiments unless otherwise stated. Distilled water was supplied from Millipore Direct Q-UV purifier for making the solutions. The powder graphite (used as adsorbent) and diazo dye (Direct Red 243) (used as target pollutant) were obtained from local companies. The chemical structure and other properties of the dye were given in Table 1.

Table 1
General characteristics of the dye

Properties	
Generic Name	C.I. Direct Red 243 (C.I. 29315)
CAS number	86543-85-3
Maximum wavelength, λ_{max}	517
Molecular formula	$C_{38}H_{28}N_{10}Na_4O_{17}S_4$
Molecular weight	1116.91
Molecular structure	Diazo class, anionic
Chemical structure	

2.1. Batch Adsorption Studies

Experimental adsorption studies were carried out in batch mode. 100 mL of dye solutions including powder graphite were introduced in glass Erlenmeyer flasks (Figure 1). Initial concentration of the dye solution was 40 mg/L for all runs. To remove dye color from solution by graphite adsorption, the flasks were put into a bath shaker (NÜVE) at ambient temperature (23°C) and mixing rate of 150 rpm.

Figure 1. Experimental setup

The dye color removal after adsorption process was determined by a spectrophotometer (HACH DR6000) at 517 nm. The removal percentage was calculated via Eq. 2.1:

$$Removal\ (\%) = \frac{(Ci - Cs)}{Ci} \times 100 \tag{2.1}$$

where; C_i and C_s were the initial and final concentrations of the dye, respectively. The adsorption experiments were repeated twice and conducted according to different levels of pH, adsorbent amount and time which were designed by Box-Behnken Design.

2.2. Batch Adsorption Studies

In this study, Box-Behnken Design, as an approach of Response Surface Methodology, was applied to investigate the effects of experimental variables on dye color removal and optimize these parameters for the highest removal. This approach of response surface methodology is comprised of a rotatable design and has one central point with three interlocking 2^3 factorials (Kumar, Prasad, & Mishra, 2007). Here, three-levels were determined for three parameters, namely, pH, adsorbent amount, and time. The design levels were shown in Table 2.

Table 2
Experimental parameters and coded/uncoded levels

Parameter	Levels			
	Coded	-1	0	+1
A: pH	Uncoded	2	6	10
B: Adsorbent Amount (g)		0.1	0.8	1.5
C: Time (min)		15	40	65

The data gained according to the design was evaluated with the statistical software, Stat-Ease® Design Expert V13. With the help of this software, ANOVA table was built up through fitting the experimental data to the linear and second-order polynomials. Also, the relations between coded and uncoded variables were presented according to the Eq. 2.2:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_{ii}^2 + \sum \beta_{ij} x_i x_j + \varepsilon \tag{2.2}$$

where β_0 is constant, β_i and β_{ij} are the effects of single parameters and two-way interactions, respectively. Also, x_i and x_j stand for the coded or uncoded single parameter levels. ε is the value of error calculated by the programme.

3. Results and Discussion

The morphological features of pristine and used graphite before/after adsorption were investigated through SEM imaging. In Fig. 2, these results were shown. For the pristine graphite (Fig. 2a-b), the surface was quite smooth and there were aggregate formation as very fine flakes. The images were in accordance with the similar studies which also presented the typical flake layered structures (Chaudhary et al., 2021; Oliveira et al., 2018). After adsorption (Fig. 2c-d), the flake layers of the graphite were preserved and any specific changes on the surface were not observed. This may be concluded to the physicochemical attachment of the dye molecules on graphite surface, which is the reason for this image.

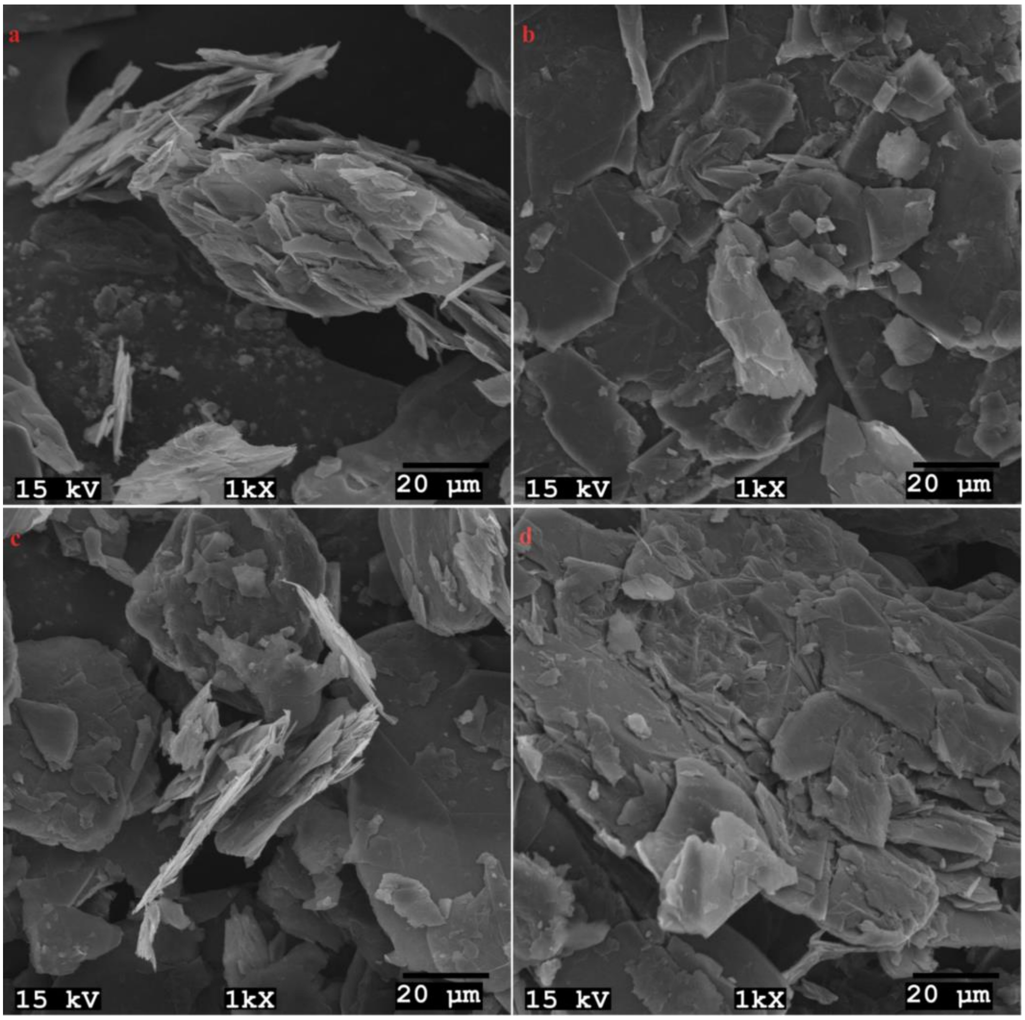


Figure 2. SEM images of graphite a-b) before and c-d) after adsorption

The design matrix and the experimental responses are listed in Table 3. All runs were repeated twice and in the table average of these results were presented. As seen from design matrix, there are three center points. The dye color removal efficiencies fluctuated between 3 and 98, which was a broader range. Despite general broadness, the efficiencies seemed to hang together around parameter groups. For example, for pH 2 and 10 or adsorbent amount 0.1 and 1.5, the difference of the effects might be perceived at first examination before the statistical analysis.

Table 3
Design matrix and dye color removal responses

Standard Run Order	pH	Adsorbent Amount (g)	Time (min)	Dye Color Removal (%)*
1	2	0.1	40	41
2	10	0.1	40	3
3	2	1.5	40	98
4	10	1.5	40	33
5	2	0.8	15	79
6	10	0.8	15	18.5
7	2	0.8	65	86
8	10	0.8	65	31.5
9	6	0.1	15	12.5
10	6	1.5	15	49
11	6	0.1	65	14.5
12	6	1.5	65	58
13-14-15**	6	0.8	40	41

***** Average values of repeated experiments were presented.

****** The average of six experiments was presented.

ANOVA was examined to understand the statistical nature of the data, as mentioned in Section 2.2. According to the Table 4, model is statistically significant (p-value < 0.05) and the insignificance of the lack of fit p-value also supports the consistence of the residuals while fitting the model. In other words, the quadratic model was adequate to resemble the fitting of the dye color removal by graphite adsorption. Also, all linear, pH-adsorbent amount interaction and square pH and square adsorbent amount terms are statistically significant. Although, pH-time and adsorbent amount-time interactions and square time terms are insignificant, they are kept in the model to preserve the insignificancy of lack of fit.

Table 4
Statistical results of ANOVA

Source	Sum of Squares	Degree of Freedom	Mean Square	F-value	p-value	Significancy
Model	21172.76	9	2352.53	252.54	<0.0001	significant
A	11881.00	1	11881.00	1275.38	<0.0001	
B	6972.25	1	6972.25	748.45	<0.0001	
C	240.25	1	240.25	25.79	<0.0001	
AB	357.78	1	357.78	38.41	<0.0001	
AC	19.53	1	19.53	2.10	0.1631	
BC	26.28	1	26.28	2.82	0.1086	
A^2	992.60	1	992.60	106.55	<0.0001	
B^2	553.33	1	553.33	59.40	<0.0001	
C^2	8.83	1	8.83	0.95	0.3418	
Residual	186.31	20	9.32			
Lack of Fit	65.19	3	21.73	3.05	0.0570	not significant
Pure Error	121.13	17	7.13			
Total	21359.08	29				
SD: 3.05 Adeq Precision: 54.62 R^2: 0.991 adj-R^2: 0.987 pred-R^2: 0.982						

The values of R^2 statistics were higher than %98. Especially, adj-R^2 (0.987) and pred-R^2 (0.982) were agreeable due to faint difference. Additionally, the value of Adeq Precision (54.62) was higher than 4 and there were enough signal to study through the design space. In Figure 3a, experimental results are paired with predicted responses. The coincidence also sustains high R^2 values. From Figure 3b, it is seen that the data points are sufficiently close to the line, which indicates the normal distribution of the residuals.

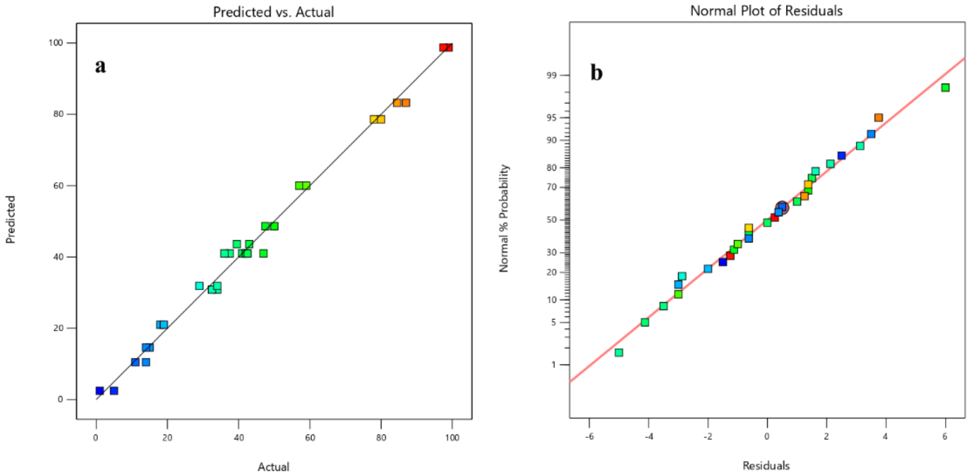


Figure 3. a) Actual vs. predicted responses b) Normal plot of residuals

The final mathematical equation of the model proposed by the software, in terms of coded and actual levels, is given in Eq. 3.1 and Eq. 3.2, respectively:

$$Dye\ Color\ Removal\ (\%) = 41.00 - 27.25xpH + 20.88xAdsorbent\ Amount + 3.88xTime - 6.69xpHxAdsorbent\ Amount + 1.56xpHxTime + 1.81xAdsorbent\ AmountxTime + 11.59xpHxpH - 8.66xAdsorbent\ AmountxAdsorbent\ Amount + 1.09xTimexTime \quad (3.1)$$

$$Dye\ Color\ Removal\ (\%) = 64.998 - 14.222xpH + 68.274xAdsorbent\ Amount - 0.162xTime - 2.388xpHxAdsorbent\ Amount + 0.016xpHxTime + 0.104xAdsorbent\ AmountxTime + 0.725xpHxpH - 17.666xAdsorbent\ AmountxAdsorbent\ Amount + 0.002xTimexTime \quad (3.2)$$

According to the Eq. 3.1, pH has the highest effect on dye color removal efficiency. The direction of the impact is in a negative way, and it can be interpreted that the efficiency may decrease in parallel to the increase in pH level. On the contrary, adsorbent amount has a positive impact that its increase supports higher removal efficiencies (Yagub, Sen, Afroze, & Ang, 2014). Here, time parameter showed no significant effect on removal compared to other two parameters, but it seems to have positive impact. Since the interaction terms of pH-time and adsorbent amount-time are statistically insignificant, only pH-adsorbent amount interaction graph is presented in Figure 4.

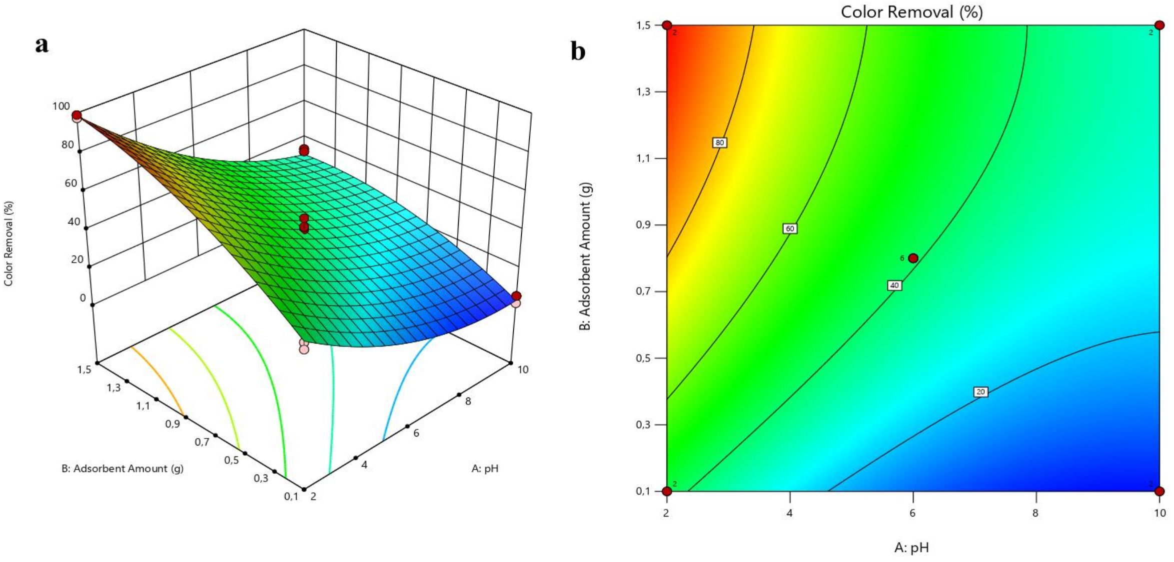


Figure 4. a) 3D surface and b) 2D contour plots of pH-adsorbent amount interaction

As seen from Figure 4a and b, the highest removal efficiencies were obtained in lowest pH levels, while the adsorbent amount is its highest. This result can be related to the nature of graphite surface under acidic conditions and to the anionic dye properties. In the acidic conditions, the graphite surface probably became positively charged and this situation led electrostatic attraction between graphite surface and anionic dye (Esmaeli et al., 2013). Also, the point of zero charge was measured in the area of pH 5.1-5.6 (Barišić et al., 2021) and it's reasonable that the surface became positively charged under this levels. Furthermore, depending on the increase in adsorbent amount, the removal efficiency was drastically improved. Probably, this was a result of increasing surface area for dye clinging as an active adsorption site (Ghaedi et al., 2015).

As seen from results, graphite shows good adsorptive efficiency for acidic dye removal, in comparison to the studies in the literature. A complex composite adsorbent showed similar efficiency (~94%) like graphite in the experimental conditions of 20 mg/L initial dye concentration, pH 4, 16 g/L adsorbent amount for 60 min (Zhang, Chen, Guo, Zhu, & Zou, 2018). Here, in this study, 98% of dye color removal was achieved in the conditions of 40 mg/L initial dye concentration, pH 2, 15 g/L adsorbent amount for 40 min.

4. Conclusion

In conclusion, graphite was found suitable alternative for the adsorption of anionic dye from aqueous solution under acidic conditions. Also, Box-Behnken Design showed good compatibility for examination of dye adsorption onto powder graphite. All the R^2 values were higher than 98%. The experimental parameters, namely, pH, adsorbent amount and time were evaluated in terms of their impacts on dye color removal. pH and adsorbent amount were concluded as the most influential but in opposite directions. Under pH 2, 98% of dye removal was achieved with 1.5 g of adsorbent for 40 min. It may be deduced that powder graphite may be a good alternative for the acidic textile effluents, which contain anionic dyes. The smooth flake structure of the pristine graphite surface was preserved after adsorption process. In comparison with other studies on graphite, the novelty of this study was its results on the efficiency of unmodified pristine graphite adsorption for dye removal to fill the gap in the literature.

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Author Contributions

Sertel Görücü: Data curation, running experiments, software, formal analysis, writing-original draft.

Çisil Gülümser: Conceptualization, methodology, data curation, software, visualization, formal analysis, writing-original draft.

Mesut Sezer: Data curation, investigation, software, writing-review and editing.

Sevil Veli: Project administration, supervision, resources, writing-review and editing.

Conflicts of Interest

The authors declare no conflict of interest.

References

Adeyemo, A. A., Adeoye, I. O., & Bello, O. S. (2017). Adsorption of dyes using different types of clay: a review. *Applied Water Science*, *7*(2), 543–568. https://doi.org/10.1007/s13201-015-0322-y

Ahmad, M. A., Eusoff, M. A., Oladoye, P. O., Adegoke, K. A., & Bello, O. S. (2020). Statistical optimization of Remazol Brilliant Blue R dye adsorption onto activated carbon prepared from pomegranate fruit peel. *Chemical Data Collections*, *28*, 100426. https://doi.org/10.1016/j.cdc.2020.100426

Barišić, A., Lützenkirchen, J., Bebić, N., Li, Q., Hanna, K., Shchukarev, A., & Begović, T. (2021). Experimental data contributing to the elusive surface charge of inert materials in contact with aqueous media. *Colloids and Interfaces*, *5*(1). https://doi.org/10.3390/colloids5010006

Berradi, M., Hsissou, R., Khudhair, M., Assouag, M., Cherkaoui, O., El Bachiri, A., & El Harfi, A. (2019). Textile finishing dyes and their impact on aquatic environs. *Heliyon*, *5*(11).

https://doi.org/10.1016/j.heliyon.2019.e02711

Bhaumik, M., McCrindle, R., & Maity, A. (2013). Efficient removal of Congo red from aqueous solutions by adsorption onto interconnected polypyrrole-polyaniline nanofibres. *Chemical Engineering Journal*, *228*, 506–515. https://doi.org/10.1016/j.cej.2013.05.026

Carvallho, M. N., Da Silva, K. S., Sales, D. C. S., Freire, E. M. P. L., Sobrinho, M. A. M., & Ghislandi, M. G. (2016). Dye removal from textile industrial effluents by adsorption on exfoliated graphite nanoplatelets: Kinetic and equilibrium studies. *Water Science and Technology*, *73*(9), 2189–2198. https://doi.org/10.2166/wst.2016.073

Chaudhary, J., Thakur, S., Mamba, G., Prateek, Gupta, R. K., & Thakur, V. K. (2021). Hydrogel of gelatin in the presence of graphite for the adsorption of dye: Towards the concept for water purification. *Journal of Environmental Chemical Engineering*, *9*(1). https://doi.org/10.1016/j.jece.2020.104762

Choudhary, M., Peter, C. N., Shukla, S. K., Govender, P. P., Joshi, G. M., & Wang, R. (2020). Environmental Issues: A Challenge for Wastewater Treatment. In M. Naushad & E. Lichtfouse (Eds.), *Green Materials for Wastewater Treatment* (pp. 1–12). Cham: Springer. https://doi.org/10.1007/978-3-030-17724-9_1

Dahri, M. K., Kooh, M. R. R., & Lim, L. B. L. (2014). Water remediation using low cost adsorbent walnut shell for removal of malachite green: Equilibrium, kinetics, thermodynamic and regeneration studies. *Journal of Environmental Chemical Engineering*, *2*(3), 1434–1444. https://doi.org/10.1016/j.jece.2014.07.008

Esmaeli, A., Jokar, M., Kousha, M., Daneshvar, E., Zilouei, H., & Karimi, K. (2013). Acidic dye wastewater treatment onto a marine macroalga, Nizamuddina zanardini (Phylum: Ochrophyta). *Chemical Engineering Journal*, *217*, 329–336. https://doi.org/10.1016/j.cej.2012.11.038

Gengec, E., Ozdemir, U., Ozbay, B., Ozbay, I., & Veli, S. (2013). Optimizing dye adsorption onto a waste-derived (modified charcoal ash) adsorbent using box-behnken and central composite design procedures. *Water, Air, and Soil Pollution*, *224*(10). https://doi.org/10.1007/s11270-013-1751-6

Ghaedi, A. M., Ghaedi, M., Vafaei, A., Iravani, N., Keshavarz, M., Rad, M., … Gupta, V. K. (2015). Adsorption of copper (II) using modified activated carbon prepared from Pomegranate wood: Optimization by bee algorithm and response surface methodology. *Journal of Molecular Liquids*, *206*, 195–206. https://doi.org/10.1016/j.molliq.2015.02.029

Khan, S., & Malik, A. (2014). Environmental and health effects of textile industry wastewater. In *Environmental Deterioration and Human Health: Natural and Anthropogenic Determinants* (Vol. 9789400778, pp. 55–71). https://doi.org/10.1007/978-94-007-7890-0_4

Kumar, A., Prasad, B., & Mishra, I. M. (2007). Process parametric study for ethene carboxylic acid removal onto powder activated carbon using Box-Behnken design. *Chemical Engineering and Technology*, *30*(7), 932–937. https://doi.org/10.1002/ceat.200700084

Lin, L., Zhai, S. R., Xiao, Z. Y., Song, Y., An, Q. Da, & Song, X. W. (2013). Dye adsorption of mesoporous activated carbons produced from NaOH-pretreated rice husks. *Bioresource Technology*, *136*, 437–443. https://doi.org/10.1016/j.biortech.2013.03.048

Malakootian, M., Mansoorian, H. J., Hosseini, A., & Khanjani, N. (2015). Evaluating the efficacy of alumina/carbon nanotube hybrid adsorbents in removing Azo Reactive Red 198 and Blue 19 dyes from aqueous solutions. *Process Safety and Environmental Protection*, *96*, 125–137. https://doi.org/10.1016/j.psep.2015.05.002

Mohebali, S., Bastani, D., & Shayesteh, H. (2019). Equilibrium, kinetic and thermodynamic studies of a low-cost biosorbent for the removal of Congo red dye: Acid and CTAB-acid modified celery (Apium graveolens). *Journal of Molecular Structure*, *1176*, 181–193. https://doi.org/10.1016/j.molstruc.2018.08.068

Oliveira, L. S., Alba, J. F. G., Silva, V. L., Ribeiro, R. T., Falcão, E. H. L., & Navarro, M. (2018). The effect of surface functional groups on the performance of graphite powders used as electrodes. *Journal of Electroanalytical Chemistry*, *818*, 106–113. https://doi.org/10.1016/j.jelechem.2018.04.022

Peng, W., Li, H., Liu, Y., & Song, S. (2016). Adsorption of methylene blue on graphene oxide prepared from amorphous graphite: Effects of pH and foreign ions. *Journal of Molecular Liquids*, *221*, 82–87. https://doi.org/10.1016/j.molliq.2016.05.074

Travlou, N. A., Kyzas, G. Z., Lazaridis, N. K., & Deliyanni, E. A. (2013). Graphite oxide/chitosan composite for reactive dye removal. *Chemical Engineering Journal*, *217*, 256–265. https://doi.org/10.1016/j.cej.2012.12.008

Veliev, E. V, Ozturk, T., Veli, S., & Fatullayev, A. G. (2006). Application of diffusion model for adsorption of azo reactive dye on pumice. *Polish Journal of Environmental Studies*, *15*(2), 347–353.

Yagub, M. T., Sen, T. K., Afroze, S., & Ang, H. M. (2014). Dye and its removal from aqueous solution by adsorption: A review. *Advances in Colloid and Interface Science, 209*, 172–184. https://doi.org/10.1016/j.cis.2014.04.002

Yetilmezsoy, K., Özçimen, D., Koçer, A. T., Bahramian, M., Kıyan, E., Akbin, H. M., & Goncaloğlu, B. İ. (2020). Removal of Anthraquinone Dye via Struvite: Equilibria, Kinetics, Thermodynamics, Fuzzy Logic Modeling. *International Journal of Environmental Research, 14*(5), 541–566. https://doi.org/10.1007/s41742-020-00275-0

Zhang, C., Chen, Z., Guo, W., Zhu, C., & Zou, Y. (2018). Simple fabrication of Chitosan/Graphene nanoplates composite spheres for efficient adsorption of acid dyes from aqueous solution. *International Journal of Biological Macromolecules*, *112*, 1048–1054. https://doi.org/10.1016/j.ijbiomac.2018.02.074