

ADSORPTION OF CATIONIC AND ANIONIC DYES FROM AQUEOUS SOLUTION USING SUNFLOWER HUSK

Huda A. Jaber¹, Marwa F. Abdul Jabbar¹, ✉

<https://doi.org/10.23939/chcht15.04.567>

Abstract. The current study deals with the removal of cationic dye (brilliant green) and anionic dye (methyl orange) from wastewater by using sunflower husk as an adsorbent. The operation takes place batch wise by applying several concentrations of the dye solution with various adsorbent amounts, at a range of initial PH values and particle sizes at varying contact time intervals. The percent of dye removed for two dyes increased with increasing time and adsorbent dose and decreased with increasing the dye concentration and particle size. The equilibrium time differed according to conditions used. The optimum removal for brilliant green dye was 98 %, which was achieved at 50 ppm dye concentration, 2 g/l adsorbent dose, 75 μm particles size and pH 7 at contact time of 1 h, compared with low removal for methyl orange that reached 54 % under optimum conditions (dye concentration 10 ppm, adsorbent dose 4 g/l, pH 3 at the same particles size and time). Kinetic studies were conducted and revealed that the adsorption was well defined by pseudo-second order model and could be described by the Langmuir isotherm.

Keywords: adsorption, sunflower husk, methyl orange, brilliant green, basic dyes, acidic dyes.

1. Introduction

The textile industry consumes huge amounts of water in wet processing operations, thus inducing essential quantities of wastewater, including large amounts of heavy metals, organic pollutants and coloring materials. Among them, the colored dyes materials cause numerous problems [1].

Dyes are main components usually used in different industries such as leather, textile, paper and plastic production [2]. These industries consume large amounts of water and result in extensive volumes of wastewater from various processes in the dyeing and

finishing steps. Therefore, the existence of small amounts of dyes in water (less than 1 mg/dm^3 for some dyes) is extremely apparent and unfavorable [3]. Color hinders the accurate entry of sunlight into water bodies, obstructing photosynthesis, preventing the growth of aquatic biota and influencing the solubility of gases within the water bodies. Dyes have been represented universally as poisonous since they cause skin, lung and respiratory problems [4].

Dyes exist in many structural forms, including anionic (reactive and acid dye), cationic (basic dyes) and nonionic dyes (vat dyes and dispersed dyes) [5]. According to dye classifications, brilliant green and methyl orange are classified as cationic and anionic dyes, which need disposal from wastewater. They are widely used in textile dyeing and paper printing and are seemed toxic for humans and animals because they harm the eyes, and their contact with skin results in irritation with pain and redness. Therefore, the dye removal is of great significance [6].

Different treatment processes have been used for the dye removal, such as adsorption [7], reverse osmosis [8], solvent extraction [9], chemical precipitation [10], ion exchange [11], ozonation [12], coagulation–flocculation and membrane process [7]. Among these methods, adsorption is the most efficient technique for elimination of organic components from the aqueous solution because of its easy design, susceptibility to noxious materials and simplicity of operation [13]. But its utilization is finite due to the adsorbents high cost and persistent problems of the regeneration. Therefore, consideration for organic pollutant removal employing substitutional low cost adsorbents is presently increasing by many researchers [14].

Various agricultural biomasses like peanut hulls [15], palm kernel fiber [16], sugarcane dust [17], wheat straw and apple pomace [18], banana peel and orange peel [19], citrullus lanatus peel [20], waste tea leaf [21], tree fern [22], Annona squamosal seed [23], coffee husk [24] and sawdust [25] have been already studied for the removal of various kinds of dyes. The employment of plant residues for the wastewater treatment has the following advantages: (i) plant residues are cellulosic compounds which have a natural capability to uptake waste chemicals such as dyes from water by means of the

¹ Chemical Engineering Department, Al-Nahrain University, Baghdad, Iraq

✉ marwa84_2007@yahoo.com

© Jaber H., Abdul Jabbar M., 2021

Eq. (2) was rearranged to Eq. (3)

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

where C_e is the concentration of the adsorbate at equilibrium, mg/l; q_e is the quantity of the adsorbate adsorbed per adsorbent mass unit and calculated from Eq. (3a), mg/g; q_m and b are the Langmuir constants, their value can be calculated graphically from intercept and slope of plotting (C_e/q_e) vs. C_e [29].

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (3a)$$

where C_0 and C_e are the initial concentration of dye and equilibrium concentration, respectively, mg/l; V is the dye solution volume, l; m is the mass of adsorbent, g.

The Freundlich isotherm is an empirical model that supposes heterogeneous adsorptive energies on the adsorbent surface. It is expressed by the following equation [30]:

$$q_e = K_f C_e^{1/n} \quad (4)$$

This equation is linearized by taking logarithms as follows:

$$\log q_e = \frac{1}{n} \log C_e + \log K_f \quad (5)$$

where K_f and $1/n$ are empirical constants. They can be determined by plotting $\log q_e$ vs. $\log C_e$, and the slope of the line is the value of $1/n$, while $\log K_f$ is the y-intercept of line.

2.4. Kinetics of Adsorption Process

For analyzing the adsorption of dye onto sunflower husks, pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models were applied to the best experimental data [31].

The pseudo-first order model is generally expressed as:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (6)$$

where q_t and q_e are the biosorption capacity of dye at time t and the equilibrium, respectively, mg/g; q_t is calculated according to Eq. (6a); k_1 is the biosorption rate constant of the pseudo-first order model.

$$q_t = C_0 - C_t \quad (6a)$$

where C_t is the remaining dye concentration at time t , mg/l.

The pseudo second-order model supposes that the adsorption follows a second-order mechanism and chemical adsorption, perhaps the rate limiting step, that includes covalent forces or valence forces between adsorbate and sorbent.

The rate of the pseudo-second order reaction is expressed by Eq. (7):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where k_2 is the pseudo-second order rate constant, g/mg·min.

The intra-particle diffusion model presumes that adsorption is a multi-step process including transfer of adsorbate from the aqueous solution to the sites of the adsorbent (surface sorption) and diffusion into pores (intra-particle diffusion) and this model is expressed as Eq. (8)

$$q_t = k_p t^{1/2} + C \quad (8)$$

where k_p is the intra-particle diffusion rate constant, mg/g·min^{1/2}; C is a constant, mg/g.

3. Results and Discussion

3.1. Effect of pH

The influence of pH on the removal of brilliant green dye by sunflower husks was considered by variations in the pH of dye solution (from pH 3 to pH 11) at the initial dye concentration of 100 ppm, particles size of 75 μm and sunflower husk amount of 2 g/l. The dye removal percentages vs. different pH values are plotted in Fig. 1.

The results indicate that the dye removal increases with increasing initial pH of the dye solution from 3 to 7 and decreases at pH 11. It was 24 % for an acidic medium, while maximum removal occurs at pH 7, which was 80 % after 50 min, and as the pH value increases to 11, the removal efficiency decreases to 66 %.

At lower pH values, the concentrations of H⁺ are high and they contend with dye cations for unoccupied adsorption sites, leading to the decrease in the dye uptake. Increasing the pH value, the surface of adsorbent is negatively charged and encourages uptake of cationic dye because of increasing electrostatic force of attraction. For a higher value (pH 11) the uptake level decreases due to the formation of a soluble hydroxyl complex between the adsorbent and the dye. This behavior agrees with Dakhil [32], who found the maximum removal of methylene blue by spent tea leaves at pH 7 and less removal for acidic and basic solutions.

The effect of pH on the removal of methyl orange dye was also studied (Fig. 2). Low removal rates were obtained for natural and basic environments while for acid systems a higher removal percent (26 %) was obtained after 40 min. This means that the sunflower husk required activation or modification to be able to adsorb more methyl orange dye from the water.

3.2. Effect of Contact Time and Adsorbent Dosage

The effect of time and adsorbent dosage on dye removal were investigated by varying the sunflower husk amount from 0.5 to 4 g/l for brilliant green and from 4 to 15 g/l for methyl orange at times ranging within 10–60 min, as illustrated in Figs. 3 and 4, respectively. The dye concentration was 50 ppm, particles size 75 μm and optimum pH solution for each dye (pH 7 for brilliant green and pH 3 for methyl orange). It was observed that the percentage of dye removal increased as time and sunflower husk dosage were increased.

It can be seen from Fig. 3 that the removal efficiency of brilliant green increased with increasing time for all adsorbent doses due to existence of free sites on the upper surface of the biosorbent and then began slowing with the gradual occupancy of these sites [3]. Equilibrium

time for each dosage differed depending on the amount of sunflower husks. It was 20 min for high amounts (2–4 g/l), while for low dosage (1 g/l) more time was needed to reach equilibrium (50 min). Also, an increase in the biomass amount from 0.5 to 2 g/l led to an increase in the removal efficiency from 58 to 96 %, after 60 min. This is due to the increase in the surface area of sunflower husk and availability of more adsorption sites, consequently making penetration of the dye to the sorption sites [33] easier. Further increases of adsorbent to 3–4 g/l showed little difference for removal efficiency; therefore, it is not economical to increase adsorbent doses greater than 2 g/l.

A similar behavior was observed for methyl orange (Fig. 4). Although the amount of sunflower husk was higher than that used for brilliant green, a lower value of removal efficiency is observed. The maximum removal efficiency was 51 % at adsorbent amount of 15 g/l (cf. with 98 % at adsorbent amount of 2 g/l for brilliant green).

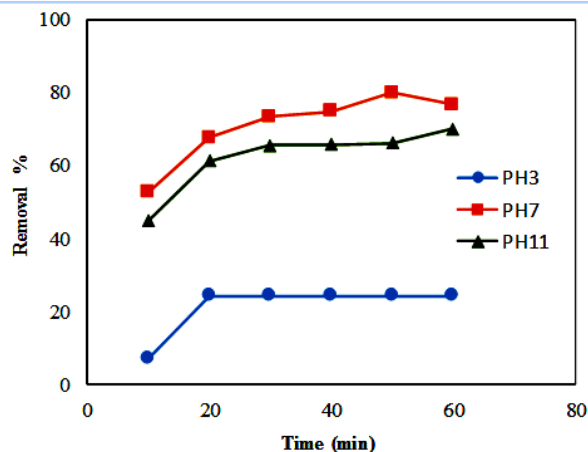


Fig. 1. Effect of pH on the brilliant green adsorption. Adsorbent dose is 2 g/l, dye concentration is 100 ppm and particles size is 75 μm

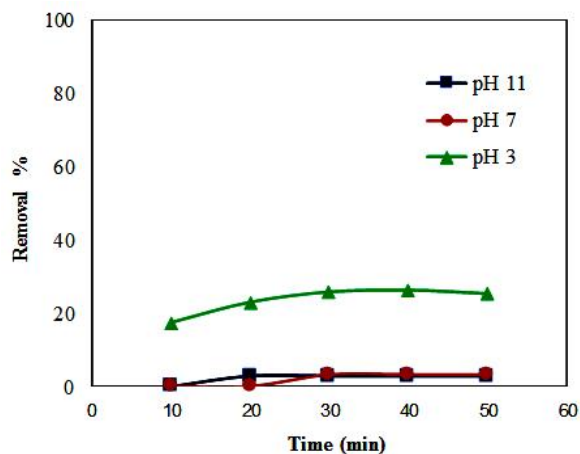


Fig. 2. Effect of pH on the methyl orange adsorption. Adsorbent dose is 4 g/l, dye concentration is 50 ppm and particles size is 75 μm

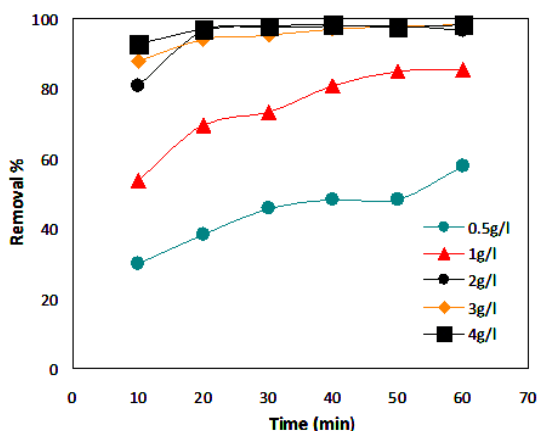


Fig. 3. Effect of sunflower husk dosage on the adsorption of brilliant green. Dye concentration is 50 ppm, particles size is 75 μm , pH 7

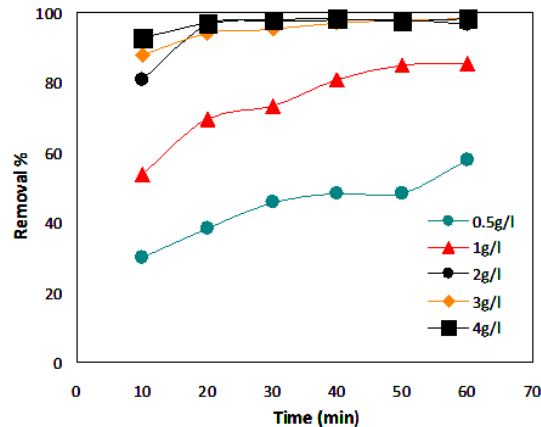


Fig. 4. Effect of sunflower husk dosage on the adsorption of methyl orange. Dye concentration is 50 ppm, particles size is 75 μm , pH 3

3.3. Effect of Adsorbate Concentration

The effect of adsorbate concentration on the dye adsorption is illustrated in Fig. 5 and 6 for brilliant green and methyl orange, respectively.

As the concentration of dye increased from 25 to 100 ppm (Fig. 5), the dye adsorbed percentage decreases from 98 to 77% after 60 min. The result denotes that the removal efficiency depends on the initial concentration of dye. This phenomenon can be explained in terms of available active sites. At low concentrations of adsorbate, the ratio of active surface sites to total dye is high; hence the dye ions could interact with the adsorbent to occupy the active sites on

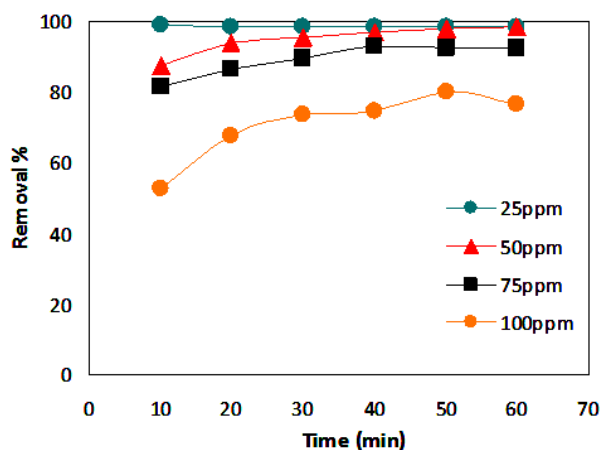


Fig. 5. Effect of adsorbate (brilliant green) concentration on the dye adsorption. Adsorbent dose is 2 g/l, particles size is 75 μ m, pH 7

3.4. Effect of Particles Size

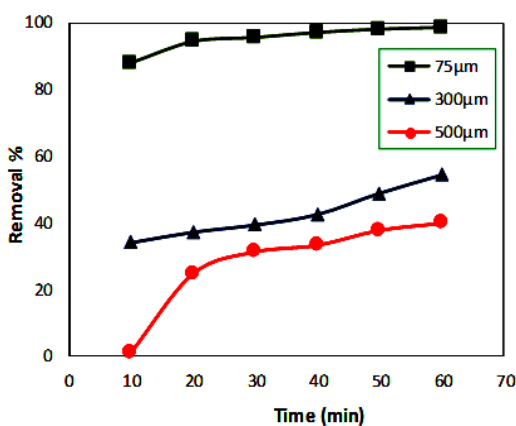


Fig. 7. Effect of particles size on the brilliant green adsorption. Adsorbent dose is 2 g/l, dye concentration is 50 ppm, pH 7

The size of the adsorbent was varied to observe the influence of particles size on a removal efficiency. Since the adsorbent was not suitable for methyl orange removal,

the sunflower husk surface and can be removed from the solution. But with the increase in adsorbate concentration, the number of active adsorption sites is not enough to contain dye ions, and this agrees with the literature data [34].

Fig. 6 represents how the methyl orange dye concentration affects the removal efficiency. After 50 min, when the concentration decreased from 50 to 10 ppm, the removal increased from 24 to 54%. Although the concentration of methyl orange was lower (10–50 ppm) than that of brilliant green (25–100 ppm), the sunflower husk was more effective for the removal of brilliant green. This means that it is not suitable for methyl orange removal.

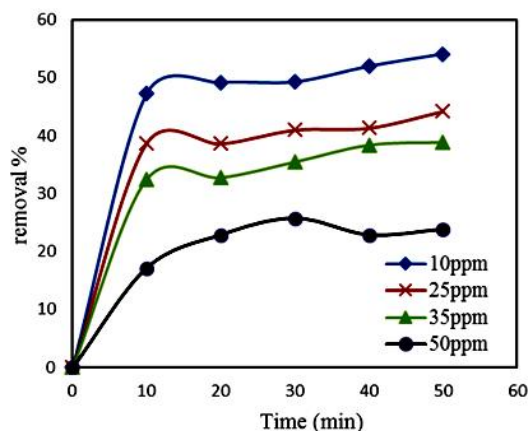


Fig. 6. Effect of adsorbate (methyl orange) concentration on the dye adsorption. Adsorbent dose is 4 g/l, particles size is 75 μ m, pH 3

the effect of its particles size was not studied. For brilliant green dye the experimental results are shown in Fig. 7 at the constant dye concentration of 50 ppm, adsorbent dose of 2 g/l and pH 7. It was noted that the smaller size gave a higher removal efficiency: 98, 54 and 40% for particles size of 75, 300 and 500 μ m, respectively, after contact time of 60 min. The reason is that a great number of smaller particles accommodates the adsorption system with a greater surface area ready for dye removal [1].

3.5. Comparison Between Cationic and Anionic Dyes

The sunflower husk was used as an adsorbent for the uptake of two types of dyes, brilliant green as a cationic dye and methyl orange as an anionic dye. The results are shown in Fig. 8 at dye concentration of 50 ppm, adsorbent dose of 4 g/l, particles size of 75 μ m and pH 7 for brilliant green and pH 3 for methyl orange.

Cationic dyes are rapidly adsorbed on the sunflower husk. After 20 min, nearly 97% of basic dyes

can be removed from water, while for anionic species only about 23 % were removed by the adsorbents. The greater attraction for the sunflower husk of cationic dyes than that of anionic dyes can be assigned to the cellulosic composition of the adsorbents.

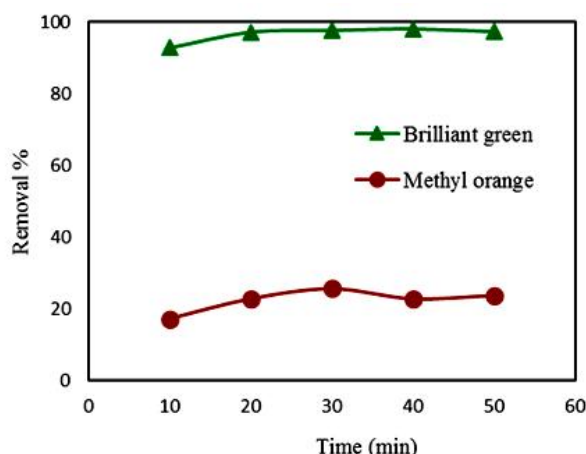


Fig. 8. Adsorption of methyl orange and brilliant green at concentration of 50 ppm. Adsorbent amount is 4 g/l, particles size is 75 μm

The coulombic forces between dye species and negatively charged cellulose in water are the main interactions which influence the dye adsorption on the sorbents. It is evident that higher adsorption rates are needed for the removal of anionic dye; the sunflower husk must be chemically modified with cationic groups.

This behavior agrees with Sun and Xu [26], who used sunflower stalks as an adsorbent for the removal of two types of cationic dyes and two types of anionic types. The higher removal percent was shown for cationic dyes (methylene blue), which was 80 %, compared with 10 % for anionic dye (congo red).

3.6. Adsorption Isotherm

The adsorption isotherm and kinetics were calculated only for the best dye removal. Therefore, the experimental equilibrium adsorption data of brilliant green onto sunflower husks have been analyzed using Freundlich and Langmuir isotherms.

The parameters of Langmuir and Freundlich isotherms and the coefficients correlation (R^2) of each isotherm were calculated by the linearized regression method and are listed in Table 2 and shown in Figs. 9 and 10, respectively. Results specified that the adsorption is described well by the Langmuir isotherm model.

Table 2

Langmuir and Freundlich parameters

Isotherm model	Parameter	Value
Langmuir	q_m , mg/g	61.728
	b , l/mg	0.711
	R^2	0.9791
Freundlich	K_f , mg/g	26.867
	n	3.054
	R^2	0.8699

3.7. Adsorption Kinetics

Three kinetic models were used in this work: pseudo-first order, pseudo-second order, and intra-particle diffusion models. Figs. 11, 12 and 13 show the application of the kinetic models by plotting $\ln q_t$ vs. t , (t/q) vs. t and q_t vs. $t^{1/2}$, respectively. To determine the degree of agreement for the kinetic model, the coefficients R^2 were determined. The highest R^2 specifies the applicability of the kinetics model.

The pseudo-second order model was more suitable to characterize the adsorption kinetic data for brilliant green, and all kinetics parameters are listed in Table 3.

Table 3

Adsorption kinetic parameters

Adsorption model	Parameter	Value
The pseudo-first order model	K_1 , min^{-1}	0.0013
	q_e , mg/g	45.6
	R^2	0.922
The pseudo-second order model	K_2 , g/mg·min	0.018
	q_e , mg/g	50
	R^2	0.9998
Diffusion model	K_p , $\text{mg/g} \cdot \text{min}^{1/2}$	0.6847
	C	43.942
	R^2	0.9634

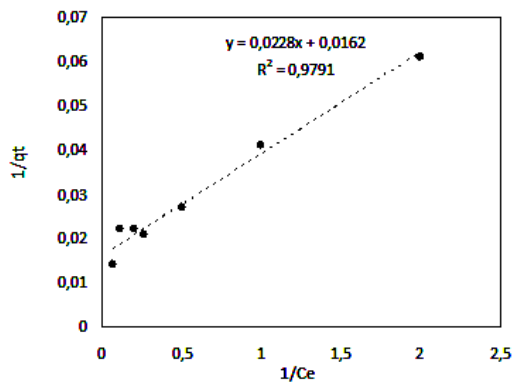


Fig. 9. Linearization of Langmuir model

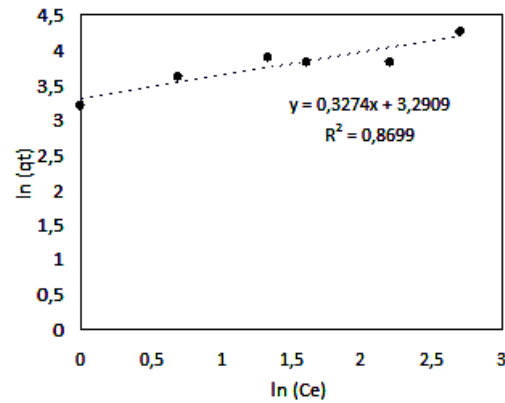


Fig. 10. Linearization of Freundlich model

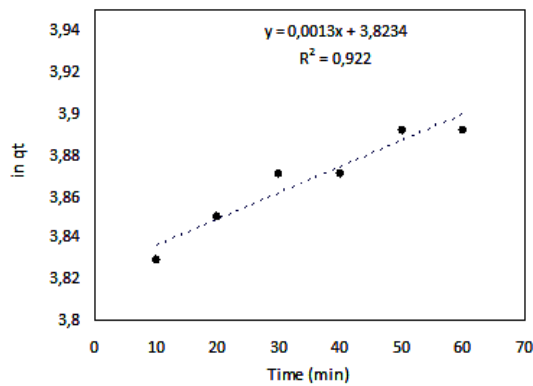


Fig. 11. Linearization of the pseudo-first order model

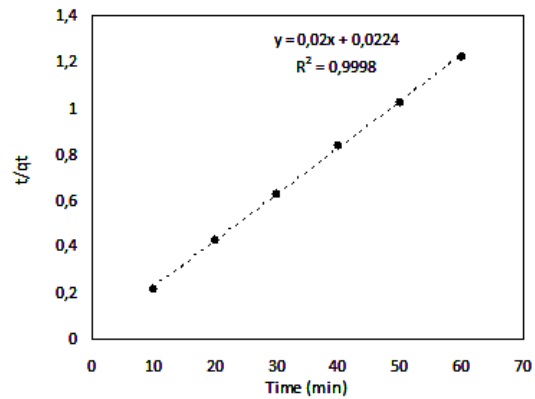
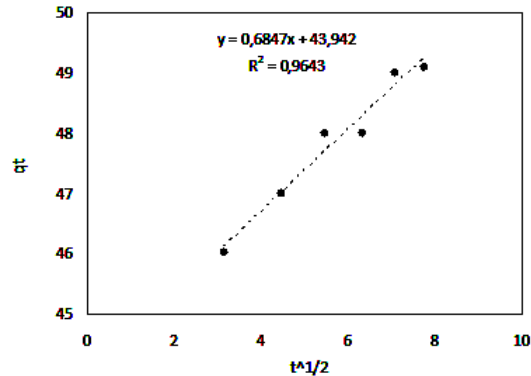


Fig. 12. Linearization of the pseudo-second order model

Fig. 13. Linearization of the intra-diffusion model



4. Conclusions

The adsorption process using sunflower husks ensures an excellent removal of brilliant green dye from water but is less effective for the removal of methyl orange dye, although the quantity of sunflower husks was high and the dye concentration was low. The best solution for brilliant green was neutral one (pH 7) since it gave high removal compared to acidic and alkaline media, while for

methyl orange the acidic medium was better than neutral and alkaline ones. The removal efficiency increases with the decrease in dye concentration and particles size. As the amount of adsorbents increases, the removal increases as a result of more available active sites. The optimum removal obtained from experiments was 98 % using the sunflower husk, with adsorbent amount of 2 g, brilliant green dye concentration 50 ppm, particles size 75 μm and pH 7. The pseudo-second order model produced a better fit than other

kinetic models and equilibrium experimental data were defined by a Langmuir isotherm model.

References

- [1] Srisorrachatr S., Sriromreun P.: AJChE, 2013, **13**, 25. <https://doi.org/10.22146/ajche.49722>
- [2] Vieira A., Santana S., Bezerra C. et al.: Chem. Eng. J., 2011, **173**, 334. <https://doi.org/10.1016/j.cej.2011.07.043>
- [3] Oguntimein G.: Adv. Res. Text. Eng., 2016, **1**, 1.
- [4] Ali A., Kovo A., Adetunji S.: JEAS, 2017, **7**, 95-107. <https://doi.org/10.4236/jeas.2017.72007>
- [5] Hashem A., Akasha R., Ghith A., Hussein D.: Energy Educ. Sci. Technol., 2007, **19**, 69.
- [6] Sun S., Wana W.: Biores. Technol., 2013, **140**, 406. <https://doi.org/10.1016/j.biortech.2013.04.116>
- [7] Walker G., Hansen L., Hana J., Allen S.: Water Res., 2003, **37**, 2081. [https://doi.org/10.1016/S0043-1354\(02\)00540-7](https://doi.org/10.1016/S0043-1354(02)00540-7)
- [8] Shaban M., Abdulla H., Mahmoud L., Ahmed A.: J. Polym. Res., 2019, **26**, 181. <https://doi.org/10.1007/s10965-019-1831-4>
- [9] Yi S., Sun G., Dai F.: Text. Res. J., 2019, **88**, 1641. <https://doi.org/10.1177/0040517517705631>
- [10] Tan B., Teng T., Omar A.: Water Res., 2000, **34**, 597. [https://doi.org/10.1016/S0043-1354\(99\)00151-7](https://doi.org/10.1016/S0043-1354(99)00151-7)
- [11] Wawrzkiwicz M., Hubicki Z.: Solvent Extr. Ion Exc., 2016, **34**, 558. <https://doi.org/10.1080/07366299.2016.1218694>
- [12] Konsowa A.: Desalination, 2003, **158**, 233. [https://doi.org/10.1016/S0011-9164\(03\)00458-2](https://doi.org/10.1016/S0011-9164(03)00458-2)
- [13] Tsui L., Roy W., Cole M.: Color. Technol., 2003, **119**, 14. <https://doi.org/10.1111/j.1478-4408.2003.tb00145.x>
- [14] Gupta V., Gupta B., Rastogi A. et al.: J. Hazard. Mater., 2011, **186**, 891. <https://doi.org/10.1016/j.jhazmat.2010.11.091>
- [15] Krowiak A., Szafran R., Modelski S.: Desalination, 2011, **265**, 126. <https://doi.org/10.1016/j.desal.2010.07.042>
- [16] Ofomaja A., Ho Y.: Dyes Pigments, 2007, **74**, 60. <https://doi.org/10.1016/j.dyepig.2006.01.014>
- [17] Ho Y., Chiu W., Wang C.: Bioresource Technol., 2007, **96**, 1285. <https://doi.org/10.1016/j.biortech.2004.10.021>
- [18] Wang X., Xia L., Tan K., Zheng W.: Environ. Prog. Sustain. Energy, 2012, **31**, 566. <https://doi.org/10.1002/ep.10582>
- [19] Chaparadza A., Hossenlopp J.: Water Sci. Technol., 2012, **65**, 940. <https://doi.org/10.2166/wst.2012.935>
- [20] Latif S., Rehman R., Imran M. et al.: J. Chem., 2019, **2019**, 1. <https://doi.org/10.1155/2019/6704953>
- [21] Nehaba S., Abdullah R., Oda A. et al.: Orient. J. Chem., 2019, **35**, 1201. <https://doi.org/10.13005/ojc/350341>
- [22] Ho Y., Chiang T., Hsueh Y.: Process Biochem., 2005, **40**, 119. <https://doi.org/10.1016/j.procbio.2003.11.035>
- [23] Santhi T., Manonmani S., Vasantha V., Chang Y.: Arabian J. Chem., 2016, **9**, S466. <https://doi.org/10.1016/j.arabj.2011.06.004>
- [24] Cheruiyot G., Maina E.: Sci. African, 2019, **5**, 1. <https://doi.org/10.1016/j.sciaf.2019.e00116>
- [25] Sahmoune M., Ouazene N.: Environ. Prog. Sustain. Energy, 2012, **31**, 597. <https://doi.org/10.1002/ep.10594>
- [26] Sun G., Xu X.: Ind. Eng. Chem. Res., 1997, **36**, 808. <https://doi.org/10.1021/ie9603833>
- [27] Efanov M., Klepikov A.: Chem. Nat. Comp., 2001, **37**, 80. <https://doi.org/10.1023/A:1017666913519>
- [28] Thinakaran N., Baskaralingam P., Pulikesi M. et al.: J. Hazard. Mater., 2008, **151**, 316. <https://doi.org/10.1016/j.jhazmat.2007.05.076>
- [29] Farah J., EL-Gendy N., Farahat L.: J. Hazard. Mater., 2007, **148**, 402. <https://doi.org/10.1016/j.jhazmat.2007.02.053>
- [30] Aksu Z., Donmez D.: Chemosphere, 2003, **50**, 1075. [https://doi.org/10.1016/S0045-6535\(02\)00623-9](https://doi.org/10.1016/S0045-6535(02)00623-9)
- [31] Suteu D., Zaharia C., Malutan T.: J. Serb. Chem. Soc., 2011, **76**, 607. <https://doi.org/10.2298/JSC100721051S>
- [32] Dakhil I.: J. Kerbala Univ., 2013, **11**, 5.
- [33] Subbaiah M., Vijaya Y., Subba R. et al.: Desalination, 2011, **276**, 310. <https://doi.org/10.1016/j.desal.2011.03.067>
- [34] Tekka T., Enyew S.: Int. J. Innovat. Sci. Res., 2014, **8**, 106.

Received: August 29, 2019 / Revised: December 09, 2019 / Accepted: May 02, 2020

АДСОРБЦІЯ КАТІОННИХ І АНІОННИХ БАРВНИКІВ З ВОДНОГО РОЗЧИНУ З ВИКОРИСТАННЯМ ЛУШПИННЯ СОНЯШНИКУ

Анотація. Досліджено вилучення катіонного (діамантовий зелений) та аніонного барвника (метилоранж) із стічних вод, з використанням як адсорбенту лушпиння соняшнику. Дослідження проводили серіями за різних концентрацій розчину барвника, кількостей адсорбенту, значень рН, розмірів частинок та при різних значеннях часу контакту. Для обох барвників встановлено, що кількість видаленого барвника збільшується зі збільшенням часу та кількості адсорбенту і зменшується зі збільшенням концентрації барвника та розміром частинок. Час встановлення рівноваги змінювався залежно від умов досліджень. Визначено, що оптимальна ступінь видалення діамантового зеленого становить 98 % за концентрації барвника 50 ррт, кількості адсорбенту 2 г/л, розмірі частинок 75 мкм та рН 7 за час 1 год порівняно з 54 % метилоранжу за оптимальних умов (концентрація барвника 10 ррт, кількість адсорбенту 4 г/л, рН 3 при однакових розмірах частинок і однаковому часі). Проведені кінетичні дослідження показали, що адсорбція визначається псевдомоделлю другого порядку і може бути описана ізотермою Лангмюра.

Ключові слова: адсорбція, лушпиння соняшнику, метилоранж, діамантовий зелений, основні барвники, кислотні барвники.