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ORIGINAL ARTICLE

Optimization of Direct Blue 71 sorption by organic rich-compost following multilevel multifactor experimental design

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KEYWORDS

Compost; Multilevel multifactor design; Low-cost adsorbent; Multi-parameter isotherm; Fixed-bed adsorber; Recycling Abstract Removal of a troublesome textile dye, Direct Blue 71 (DB71) from water by a food waste compost was assessed in the current study. Since compost dye sorption is a multi-factor process influenced by mass, pH, concentration, temperature, contact time, and salinity, the cumulative influence of all parameters on DB71 removal was examined following an optimal multilevel multi-factor experimental design. The process had to be presented using both linear and interaction terms, according to the variables analysis: Dye sorption = -0.050Mass + 0.122Conc-0.114pH + 0.132 Time $- 0.074Temp + 0.056Sal + 0.103Mass \times Conc + 0.226$ Mass $\times pH - 0.257Mass \times$ Time $- 0.112Mass \times$ Temp $- 0.041Mass \times$ Sal $+ 0.008Conc \times pH + 0.100Conc \times$ Time $+ 0.089Conc \times$ Temp $+ 0.167Conc \times$ Sal $- 0.245pH \times$ Time $- 0.231pH \times$ Temp $- 0.123pH \times$ Sal + 0.358 Tim \times Temp $+ 0.355Tim \times$ Sal $- 0.045Temp \times$ Sal (R² = 0.9241)

Salinity and pH were positively correlated with concentration, and contact time with temperature and salinity, to get better dye uptake. The optimal conditions for dye removal were the following: solid:liquid ratio 1:375, pH 3.0, initial dye concentration 400 mg L⁻¹, contact time 240 min, salinity 0.6 M NaCl, temperature 50 °C. At the optimum combination of factors, equilibrium sorption isotherm and sorption kinetics were studied. Kinetic analysis indicated high sorption rate 4.0 mg g⁻¹ min⁻¹ while 28% of maximum capacity was reached within the first 10 min of interaction. Sorption isotherm has L2-shape which reflected surface saturation at high solute concentration with low competition with solvent molecules, with a maximum sorption capacity of 95.4 mg g⁻¹. In column

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experiments performed at bed depth 5.1–12.8 cm, flow rate 1.0–2.0 mL min⁻¹ and influent concentration 10–20 mg L⁻¹, sorption capacity was 19.6 mg g⁻¹, which represents 21% of the maximum capacity at equilibrium conditions. IR analysis of dye-loaded-compost confirmed the contribution of hydrophobic-hydrophobic forces in the sorption process.

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1. Introduction

Before the coming of synthetic colorants, the main sources of coloration were insects and flowers. At the end of the 19th century, the preparation of the first synthetic dye, Mauveine, started the dyeing industry thank to its ability to facilitate large scale production (Mudhoo et al., 2020). Aspects such as high colour brightness, enhanced colouring strength, and costeffectiveness made synthetic dyes an important class of chemicals applied in the textile industry (Raval et al., 2017). Currently, a large number of synthetic dyes are commercially applied in numerous applications: it has been estimated that 10,000 different textile dyes are available worldwide with annual production of 7×10^5 ton (Lalnunhlimi et al., 2016). There are different classes of dyes according to their source (natural or synthetic), chemical structure (azo, nitro and nitroso, anthraquinone, polycyclic aromatic carbonyl and polymethine) and fabric application (acidic, direct, reactive, basic and disperse) (Kausar et al., 2018). Among textile dyes, azo dyes are often applied to colour acrylic, polyesters cotton, rayon, and other cellulosic fabrics (Kausar et al., 2018; Tripathi, 2019). The structure of azo dyes may contain one to four azo groups (N = N), known to resist degradation and hence accumulate in the aquatic environments (Benkhaya et al., 2020).

The extensive use of synthetic dyes in industrial coloration produces water pollution with substances that are hazardous (carcinogenic and/or mutagenic) to humans and have undesired aesthetical effects (Kausar et al., 2018; Tripathi 2019). Moreover, textile effluents along with tannery wastewaters are known of their building up chemical oxygen and biological demands (Tripathi et al., 2009; Barsova et al., 2019). Thus, treatment of wastewaters polluted with textile dyes is essential for the environment. Advanced oxidation, flotation, photocatalytic cleaning are among the methods used for dye removal solution (Montazerozohori & Jahromi, 2012; from Montazerozohori and Malekhoseini, 2015; Ertugay & Acar, 2017; Kyzas & Matis, 2018). Compared to flocculation, coagulation and biological treatment methods, adsorption by activated carbon has been reported to be the most effective for the removal of reactive, acid, basic and direct dves, while ozonation showed limited application only for direct dyes (Fu & Viraraghavan, 2001). In fact, adsorption by activated carbon is a preferred cleaning method toward all classes of textile dyes due to high affinity, adaptability, ease of application, and economic/industrial practicality. However, its high cost can eventually prevents its use and the search for alternative low-cost materials that can be used as adsorbents is an active field of research. In this sense, compost has been reported as a costeffective media for removal of heavy metals and organics (Paradelo & Barral, 2012; Anastopoulos & Kyzas, 2015; Paradelo et al., 2019, 2020; Mudhoo et al., 2020). Compost

is a brown to dark stabilized organic matrix produced under controlled aerobic microbial exothermic degradation process of organic wastes. The stages of composting under normal conditions are (Manu et al., 2017; Ma et al., 2018; Guo et al., 2019): a) mesophilic step in which decomposition is achieved under moderate temperatures by mesophilic microorganisms, b) thermophilic step in which decomposition process accelerated by thermophilic bacteria and at higher temperatures (up to 60 °C), and c) maturation step in which temperature is declined and the mesophiles once again predominate to reach the final maturation phase. Composts are often directed for agronomical purposes, however, its application for the removal of textile dyes has been receiving increasing attention in the literature (Paradelo et al., 2019, 2020; Al-Zawahreh et al., 2021). Although composts do not have a high porous surface like activated carbon, the presence of functional groups (carboxylic, carbonyl, and amino groups) was the reason of their application in water treatment (Mudhoo et al., 2020). Application of composts as adsorbents is especially indicated for those not suitable for agronomic purposes, due for example to low nutrient contents, high salinity or high levels of metals (Paradelo & Barral, 2012; Paradelo et al., 2019, 2020).

Interaction of organic dyes with compost is a multiparameter processes influenced by factors such as adsorbent:solution ratio, particle diameter, dye concentration, solution pH, salinity, contact time or temperature. Optimization of experimental factors by the classical method involves modifying one factor while maintaining others constant (Brereton, 2007; Tanyildizi, 2011; Akar et al., 2014). This method may be effective in some cases, but it consumes energy, time, and materials/reagents when testing high number of factors, as a large number of experimental tests are need to find out the effect of each single factor on the entire sorption process. Such limitations of single-factor method can be handled by optimizing all operating factors following appropriate experimental deigns (Brereton, 2007; Tanyildizi, 2011; Akar et al., 2014). Box-Behnken design, central-composite design or multilevel multifactor design have been used to optimise multi-factor systems for the adsorption of phthalate esters by humic acid (Abdelghani et al., 2019), diuron by date pits (Al-Degs et al., 2013), decolorization by modified biomaterial (Akar et al., 2014), methylene blue, acid orange 52 and disperse orange 30 by activated carbon (Tan et al., 2008; Ahmad et al., 2009; Tripathi et al., 2009), reactive dyes sorption by peanut hull (Tanyildizi, 2011), or methylene blue adsorption by modified activated carbon (Ghalehkhondabi et al., 2021).

Although some research works have dealt with the uptake of dyes by compost, multivariable optimization has not been considered yet in the literature. In this work, the sorption of a weakly interacting dye, Direct Blue 71 (DB71) by a food waste compost is examined under various experimental conditions. The effect of six variables (mass, concentration, pH, temperature, salinity, and contact duration) was investigated using an orthogonal multilevel multifactor experimental design, with the objectives of advancing in the knowledge of the factors that control dye removal and finding the best conditions for the process. Kinetics, equilibrium, and column tests were performed at the optimal sorption conditions based on the outputs of multifactor design, the data are presented by several sorption models, and the sorption mechanism of DB71 is discussed.

2. Experimental methodologies

2.1. Compost

The compost employed in the study was kindly donated by Irbid Composting Plant (Irbid, Jordan). Briefly, the compost was produced under aerobic conditions from 700 kg of Nrich vegetables including tomato, cabbage, and radish, blended with 300 kg of C-rich branches of olive and cypress trees, previously chopped and air-dried. The pile was turned over on a daily basis to avoid rising temperature above 60 °C and prevent ash formation in the final product. The process of pile mixing continued until the temperature stabilized around 25 °C for few days, which required approximately 70 days from the start of composting. The final compost was mechanically sieved, air-dried, and packed in plastic bags for the experiment and chemical analysis.

The final compost presented a particle size over the range 50–2000 μ m, with the fraction < 106 μ m accounting for 39% of the bulk sample. Solution pH, pH_{ZPC}, electrical conductivity, ash content, moisture content, soluble P, K and heavy metal contents were determined as described in previous works (Al-Degs et al., 2008; Al-Zawahreh et al., 2021). C, H, and N were quantified using a CHN elemental analyser (ELTRA CW multiphase determinator, Italy). Specific surface area was measured following methylene blue adsorption test (Yener et al., 2012). Fourier transform infrared (FTIR) spectra were measured on a Bruker spectrophotometer (Bruker, Germany) using pellets prepared by mixing 3.0 mg of compost with 300.0 mg of KBr under vacuum. To minimize moisture influence, pellets were heated at 105 °C for 24 hr before measurement. The spectra of dye-loaded-compost was also measured to elucidate the mechanism of interaction with the surface. All spectra were presented over the 400 to 4000 cm^{-1} with a resolution of 2 cm⁻¹. For identical presentation of samples, spectra were baseline corrected and normalized in absorbance.

2.2. Adsorbate

Direct Blue 71 (Fig. 1) was purchased from Sigma–Aldrich® chemicals with purity > 99.5%. The dye was quantified at 584 nm with a dynamic range (1.0–85.0 mg L⁻¹), detection limit 0.3 mg L⁻¹, and quantification limit of 1.0 mg L⁻¹. DB71 is visible in down to 0.5 mg L⁻¹.

A standard solution of 500 mg L⁻¹ was prepared by dissolving an accurately weighed quantity of the dye in deionized water and subsequently diluted to the needed concentrations. The pH of dye solutions were adjusted to the desired value using 0.15 M HCl and 0.15 M NaOH solutions. The p K_a of DB71 was determined by potentiometric titration: 0.010 M dye solution (at pH = 2.0) was titrated immediately with 0.11 M NaOH. During titration, volume of titrant and pH were recorded. Acidity constant pK_a was determined from the half-titration-point of pH- V_{NAOH} plot.

2.3. Design of experiments, factors coding, and optimization sorption process

Following a multilevel multifactor design, the optimum combination of factors leading to the best dye uptake with minimum experimental efforts can be determined. The combined influence of six factors (sorbent mass, pH, concentration, contact time, temperature, and salinity) on DB71 retention by compost was studied using a balanced multilevel multifactor design (Brereton, 2007). Multilevel multifactor design is necessary to save time while studying the influence of all factors on dye retention by running limited number of tests. Moreover, the factorial design can detect the possible interaction between factors. The proper selection of the levels of the factors and coding of these levels is necessary to end up with meaningful outputs. Four levels for each factors were selected and coded as -2, -1, +1, and +2 (the selected levels along with codes for the factors are provided in Table 1). Coding of levels is necessary because of the high numerical differences between levels from factor to factor, so coding allows to balance these variations and improve modelling quality. To generate an orthogonal design, the proper number of experiments N must be a



Fig. 1 Chemical structure of Direct Blue 71 $\underline{C_{40}H_{23}N_7Na_4O_{13}S_4}$ (p K_a 2.71).

Code	Factor (unit)				Levels					
					-2		-1	+1	+2	
X ₁	Mass	s (g)			0.20		0.40	0.60	0.80	
X ₂	Conc	entration (1	ng L^{-1})		200		300	400	500	
X ₃	pН				3.0		5.0	7.0	9.0	
X_4	Cont	act time (hr	;)		60		120	180	240	
X ₅	Temp	perature (⁰ C	C)		20.0		30.0	40.0	50.0	
X ₆	Salin	ity (M)			0		0.3	0.6	0.9	
Sorption test ^a	\mathbf{X}_1	X ₂	X ₃	X_4	X ₅	X_6	Experimental value (mg/g)	Sorption	Predicted Sorption value (mg/g)	
1	2	-2	-2	-2	-2	-2	12.9		12.1	
2	$^{-2}$	-1	-1	2	-1	-2	16.4		27.6	
3	-1	-1	2	-1	$^{-2}$	1	22.4		22.2	
4	-1	2	-1	-2	1	1	24.5		31.6	
5	2	-1	-2	1	1	-1	11.7		25.7	
6	-1	$^{-2}$	1	1	-1	1	24.8		22.4	
7	$^{-2}$	1	1	-1	1	-2	11.5		18.4	
8	1	1	-1	1	$^{-2}$	2	68.7		48.6	
9	1	-1	1	-2	2	2	12.8		11.1	
10	-1	1	-2	2	2	1	91.3		64.9	
11	1	$^{-2}$	2	2	1	2	10.8		24.7	
12	-2	2	2	1	2	-2	27.7		23.0	
13	2	2	1	2	$^{-2}$	-1	44.6		36.0	
14	2	1	2	-2	-1	-1	14.6		24.0	
15	1	2	-2	-1	-1	2	51.8		52.2	
16	2	-2	-1	-1	2	-1	9.5		8.2	

 Table 1
 Four-level six-factor factorial experimental design matrix along with experimental and predicted sorption values of DB71 by compost.

^a For a multilevel multilector design, number of experiments = l^2 where *l* is number of selected levels of the factors. Each test was repeated three identical times (n = 3).

multiple of a power of the number of levels l so that $N = k l^r$, where r is at least 2 (Brereton, 2007). Setting k equal to 1 and r to the minimum value, this implies that $N = l^2$. Hence for a four-level design, 16 experiments should be performed.

Sixteen tests were carried out to determine the best combination of the six factors giving the maximum retention of DB71 by compost. It is common in factorial analysis to model experimental data by building a relationship between the factors or *x*-independent variables (mass, pH, temperature, salinity, contact time, etc.) and *y* dependent variables or dye sorption value. A typical model between factors (independent variables) and dye sorption (dependent variable) is numerically provided as:

Linear terms (b₁-b₆) allow for a direct relationship between dye sorption and a given factor. The factor with higher coefficient has higher linear effect on dye uptake. For example, if $b_1 > b_2$ ($b_1 \& b_2 > 0$) then dye sorption is strongly correlated with mass compared to concentration. In the same line, positive coefficient reflected a direct correlation of the factor with sorption and vice versa. Interaction terms b_1b_2 - b_5b_6 (often significant for modelling sorption systems) are necessary to understand the nature of interaction between factors. For example, solute retention at low pH and high compost mass may be higher than at the same mass and higher pH and this can figured out by interaction terms of both factors. In fact, influence of two factors (pH and temperature for example) on solute retention is rarely independent. For example, if $b_{12}\gg b_{13}$ ($b_{12}\&b_{13} > 0$) then interaction between mass and concentration is more significant than mass and pH. Moreover, negative interaction coefficients indicate better sorption if both factors are maintained at their opposite limits. Initial analysis indicate that non-linear terms (mass × mass, pH × pH, Time × Time, etc.) were not significant for dye uptake hence excluded from Eq. (1) (Brereton, 2007).

Student's t-test was applied to assess the significance of all terms (b_1-b_{56}) provided that number of tests (16) were more than number of factors (6) (Brereton, 2007). The significance t-test was carried out as follows (Brereton, 2007): (a) the square covariance matrix was calculated and the variances (v) (the diagonal values of covariance matrix) were obtained, (b) the error sum of squares S_E were calculated from the experimental sorption values and the ones predicted from Eq. (13), (c) estimation of mean error sum of squares (s) by dividing S_E by the number of degrees of freedom which equals to N-P, where N is number of experiments (16) and P is the number of factors (6), and (d) estimation of t-value, $t = b/(sv)^{1/2}$ and the higher this ratio, the more significant is the factor at the desired confidence level. For all terms, the calculated t value was < 0.003 confirming the statistical significance of all coefficients ($t_{table} = 1.81$ at df 10 and 90% confidence level, Appendix 1).

2.4. Adsorption experiments

Based on the outputs of multifactor design, the optimum levels of tested factors will be ascertained and used to conduct kinetic, sorption, and column tests. All tests employed airdry sieved compost ($\leq 106 \ \mu$ m). Batch tests were performed by agitating 0.400 g dry compost with 150.0 mL solution of DB71 covering the concentration range (5–400 mg L⁻¹) in a thermostated shaker (GFL, Germany) at 50 °C and pH 3.0 for 240 min. In all tests, particle diameter was $\leq 106 \ \mu$ m. Compost particles were removed by centrifugation at 5000 rpm for 5.0 min and the supernatant was filtered for analysis. Dye concentration in the extract (C_e , mg L⁻¹) was determined in a UV/ VIS spectrophotometer at 584 nm. The amount adsorbed by compost (q_e , mg g⁻¹) was calculated as:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{2}$$

where C_o , V and m are initial dye concentration (mg L⁻¹), solution volume (L), and compost mass (g), respectively.

Sorption kinetics were studied by suspending 0.400 g of adsorbent in 150.0 mL of 100 mg L⁻¹ dye solution. The suspensions were then agitated for different times (5–240 min) at 50 °C, pH 3.0 and 0.6 M NaCl. At each time, 2.0 mL of the solution were withdrawn and filtered to measure its absorbance and afterwards returned to the original solution. For comparison purposes, sorption capacity of the tested compost was compared with a commercial Spanish compost toward DB71. The Spanish compost was derived from municipal solid waste MSWC which known to have a high affinity for direct dyes (Al-Zawahreh et al., 2021). In addition to DB71, sorption capacity of the local compost which also derived from municipal solid waste was also tested for Direct Blue 151. Chemical properties of MSWC and DB151 have been described elsewhere (Al-Zawahreh et al., 2021).

2.5. Desorption of dye

In order to assess potential recycling of the sorbent, 400 mg of compost were agitated with 15 mL of 400 mg L⁻¹ solution of DB71 (pH 3.0, 0.6 M NaCl, and 50 °C) in 250 mL-conical flask for 4.0 hr. The supernatant was then removed and the dyeloaded compost re-suspended in 15 mL of different solvents (0.1 M HNO₃, *n*-Hexane, H₂O, 0.1 M NaOH, and ethanol) for 4.0 hr and treated as described earlier. Desorption cycles with water was performed at the conditions (pH 3.0, 0.6 M NaCl, and 50 °C), whereas desorption by other solvents was performed at 25 °C without adjusting pH or adding salt. This procedure was repeated for two more cycles using fresh solvents and DB71 was measured in the extracts after each desorption cycle. Percentage of dye desorption was estimated from the retained amount and the amounts removed in the consecutive desorption cycles.

2.6. Fixed bed column adsorber tests

In practice, the column type continuous flow operation is more useful in large-scale wastewater treatment, easy to run, attain a high yield and can be easily scaled up from a laboratory-scale procedure (Al-Degs et al., 2009). The stages in the separation process in column adsorber can also be automated and high degrees of cleaning can often be achieved in a single step process. Column tests were carried out on a glass column with internal diameter of 1.0 cm internal diameter and 20 cm height, filled with a known amount of compost (3.0–7.0 g or bed-depth 5.1-12.8 cm). In order to provide a uniform inlet flow, a layer of glass beads was placed at the top of the packed compost. The tests were carried out by pumping dye solution through the column in downward flow mode using a peristaltic pump (Smith and Nephew Watson-Marlow, England). All experiments were conducted at 20-22 °C, pH 3.0, and 0.6 NaCl. The effect of various operational factors including flow rates (1.0, 1.5 and 2.0 mL min⁻¹), bed-depth height (5.1, 8.8 and 12.8 cm) and influent DB71 levels (10, 15 and 20 mg L^{-1}) have been investigated. The concentration of dve was measured in effluent solution which periodically collected in 5-mL glass vials. The column is considered to be essentially exhausted when the effluent concentration reaches 90% (i.e., C_{effluent}/ $C_{influent} = 0.9$ or 0.95) of initial concentration and the breakthrough point when $C_{eff}/C_{inf} = 0.01$.

2.7. Mathematical manipulation of sorption data

2.7.1. Sorption kinetics

Different kinetic equations were tested to present data including kinetic-based (pseudo first and pseudo second order) and diffusion-based (intraparticle diffusion) models. Pseudo-first and second order models are defined by Eqs. (3) and (4), respectively (Ho & McKay, 1998; Kushwaha et al., 2013):

$$q_t = q_e (1 - e^{-k_1 t}) \tag{3}$$

$$q_t = \frac{tk_2 q_e^2}{1 + tk_2 q_e} \tag{4}$$

where q_t and q_e are the amounts of dye removed at time t and equilibrium time, respectively while $k_1 \pmod{1}$ and $k_2 \pmod{1} \exp^{-1} \min^{-1}$ are the first and second order rate constants. Higher values of k_1 and k_2 reflects faster sorption kinetics (Ho & McKay, 1998).

The intraparticle diffusion equation is presented as (Weber & Morris, 1963; Kushwaha et al., 2013):

$$q_t = k_d t^{1/2} + C \tag{5}$$

where $k_d \,(\text{mg g}^{-1} \text{min}^{-1})$ and C (mg g⁻¹) are the intraparticle diffusion rate constant and the intercept, respectively.

2.7.2. Adsorption isotherms

Equilibrium data was presented by different models including two and three-parameter models (Kushwaha et al., 2013; Ayawei et al., 2017; Al-Ghouti & Daana, 2020). The models were tested to predict the dye maximum uptake capacity, formation of multilayer sorption, variability of active sites, and heterogeneity of the compost. Among two-parameter models, three models were applied (Kushwaha et al., 2013; Ayawei et al., 2017; Mariyam et al., 2021).

Langmuir equation:

$$q_e = \frac{Q_L K_L C_e}{1 + K_L C_e} \tag{6}$$

where Q_L (mg/g) and K_L (L/mg) is the maximum sorption capacity the affinity constant of the dye toward the compost. The model assumes equal-energy active sites, no interaction with adsorbed solutes, and one mono-layer coverage (Ayawei et al., 2017; Al-Ghouti & Daana, 2020). This model has been applied for many systems including dye-compost systems.

Freundlich equation: Freundlich isotherm model expression defines the heterogeneity of the surface as well as the exponential distribution of the active sites and the active sites energies (Ayawei et al., 2017).

$$q_e = K_F C_e^{1/n_F} \tag{7}$$

 K_F (L g⁻¹) is Freundlich constant and can indicate uptake capacity while 1/n measures favourability of the process and both are system specific constants (Ayawei et al., 2017). This model is common to present adsorption data for heterogeneous surfaces (including composts) over wide concentration range (Anastopoulos & Kyzas, 2015).

Sips equation: A combination of both Langmuir and Freundlich isotherm models resulted in the Sips model, which is used to predict the heterogeneity of the adsorption systems as well as to avoid the limitations associated with the increased concentrations of adsorbate in the Freundlich model (Sips, 1948; Kushwaha et al., 2013). Sips model has the validity in localizing the adsorption without the adsorbate–adsorbate interaction (Al-Ghouti & Daana, 2020):

$$q_e = \frac{Q_S K_S C_e^{n_S}}{1 + K_S C_e^{n_S}}$$
(8)

where Q_s (mg g⁻¹), K_s (L mg⁻¹)^{ns}, and n_s are Sips maximum adsorption capacity (mg g⁻¹), Sips equilibrium constant, and the model exponent, respectively (Sips, 1948; Al-Ghouti & Daana, 2020).

2.8. Estimation of sorption parameters and selection of the optimum models

The parameters of isotherms and kinetic models were estimated using non-linear regression analysis. Non-linear regression analysis was carried out using Solver toolbox which operates under Excel® program. Relative error of prediction (*REP%*) was used as a criterion to select the optimum model as equilibrium data was fitted by more than one model. *REP* % is estimated as:

$$REP\% = 100 \times \left(\frac{\sum_{i=1}^{n} (q_{i,pred} - q_{i,act})^2}{\sum_{i=1}^{n} (C_{i,act})^2}\right)^{1/2}$$
(9)

where $q_{i,pred}$, $q_{i,act}$, and *n* are predicted sorption value, actual sorption value, and number of experimental points. Lower *REP*% indicated better model fitting to the data (Chen, 2015; Ayawei et al., 2017).

2.9. Sorption by fix-bed adsorber

The total amount of retained dye in the column is dependent on the influent concentration and is estimated as follows (Han et al., 2009):

$$q_{column} = \frac{C_0 F}{m \times 1000} \int_0^t \left(1 - \frac{C_{effluent}}{C_{influent}} \right) dt \tag{10}$$

where $q_{column} \pmod{g^{-1}}$ presents the amount of removed dye at saturation time, C_{effluent} and C_{influent} are effluent and influent dye concentration (mg L⁻¹) respectively, F flow rate

(mL min⁻¹), m mass of compost (g), and t is the sorption time at saturation. Column capacity (q_{column}) is measured at different loadings of compost, flow rate, and influent concentration. For practical purposes, column capacity is often measured at 90% saturation (i.e., $C_{\text{effluent}} \approx 0.9 C_{\text{influent}}$).

3. Results and discussion

3.1. Characterization of the compost

The main physicochemical properties of the compost are shown in Table 2. It is an alkaline, organic matter rich compost with very low metal levels, as typical of composts produced only from vegetal material. Determination of pH_{zpc} allows detecting the nature of the net surface charge of the adsorbent in solution. pH_{pzc} was 8.2, hence, at solution $pH \gg 8.2$ the net surface charge is negative while positive at $pH \ll 8.2$. However, the compost presents an excessive salinity that would be a problem in agriculture or horticulture, so its use in wastewater remediation would be interesting. Given the potential agronomical applications of composts, their use for remediation processes should be restricted to those presenting some agronomic limitation, such as high salinity of pollutant contents (Paradelo et al., 2019).

The adsorbent has large surface area $(263 \text{ m}^2 \text{ g}^{-1})$ furnished with acidic functional groups which can facilitate attraction of dye from solution. The spectra of raw compost is shown in Fig. 2, with similar IR peaks as those identified in other composts. After compost maturation, the predominance of the peaks/bands at 3413 (broad band), 1623, 1411, 1029 (broad band), and 873 (short and sharp peak) cm⁻¹ are often reported (El-Ouaqoudi et al., 2015). The earlier bands/peaks indicate the richness of the composts with aromatic, phenolic, aliphatic and polysaccharide structures. The broad band at 3413 cm⁻¹ indicates the presence of carboxylic groups that generated upon oxidation of organic material during composting process. The degree of compost maturity can be assessed by estimating aromaticity indexes 1623/2862 ($v_{C=C}$ aromatic, v_{COO} /

Table 2 Physicochemical parameters of compost understudy.pHZPC: pH at point of zero charge; EC: electrical conductivity;SSA: specific surface area.

Parameter	Value
рН	8.6
pH _{ZPC}	8.2
EC, dS m^{-1}	7.8
Ash, wt%	21.7
Moisture, <i>wt%</i>	28.7
Organic Matter, wt%	76.6
P, mg kg ^{-1}	0.4
K, mg kg ^{-1}	2.9
Ni, mg kg ⁻¹	7.9
Pb, mg kg ^{-1}	9.8
Cd, mg kg ^{-1}	0.8
C, %	46.83
Н, %	4.15
N, %	1.87
C/N ratio	25
SSA m ² g ⁻¹	263



Fig. 2 FTIR scans of compost and dye-loaded compost.

 $v_{\rm C-H \ aliphatic}$) and 1623/2916 ($v_{\rm C=C \ aromatic}/v_{\rm C-H \ aliphatic}$): the values were 0.90 and 0.92, respectively, indicative of high degree of aromaticity in the final compost (El-Ouaqoudi et al., 2015). The bands at 1029 and 873 cm⁻¹, which correspond to O-CH₃ and C-H bond starching and bond waging, respectively, also show the stable organic matrix of the compost.

3.2. Optimum experimental conditions for dye uptake

As shown in Table 1, maximum retention of DB71 in the experiments extend from 9.5 mg g⁻¹ (test 16) up to 91.3 mg g⁻¹ (test 10). The lowest retention values were observed in the tests 1, 5, 7, 9, 11, 14 and 16 (<15 mg g⁻¹). The tests 3, 4, 6, and 12 produced moderate retention by the compost (22–28 mg g⁻¹), whereas higher adsorption (45–91 mg g⁻¹) was observed in the 8, 10, 13, and 15 tests. The adopted design covered all possible combinations among factors, as shown by the high variation in the measured retention values. Regression analysis indicated that linear terms (b₁-b₆, Eq. (1)) were not satisfactory to present the sorption process.

As shown in Fig. 3, including interaction terms (b_{12} - b_{56} , Eq. (1)) has improved prediction of DB71 sorption with R^2 of



Fig. 3 Prediction of DB71 sorption using linear and interaction terms (Eq. (11)).

0.9241 compared to 0.6439 for linear terms only. In fact, interaction terms can account for either synergistic or nonsynergistic effects among variables. The correlation between dye retention (dependent response) and operational factors (independent variables) are presented as:

 $\begin{array}{l} \text{Dye sorption} = -0.050 \text{ Mass} + 0.122 \text{ Conc} -0.114 \text{ pH} \\ + 0.132 \text{ Time} -0.074 \text{ Temp} + 0.056 \text{ Salinity} \\ + 0.103 \text{ Mass} \cdot \text{Conc} + 0.226 \text{ Mass} \cdot \text{pH} -0.257 \text{ Mass} \cdot \text{Time} \\ - 0.112 \text{ Mass} \cdot \text{Temperature} -0.041 \text{ Mass} \cdot \text{Salinity} \\ + 0.008 \text{ Conc} \cdot \text{pH} + 0.100 \text{ Conc} \cdot \text{Time} + 0.089 \text{ Conc} \cdot \text{Temp} \\ + 0.167 \text{ Conc} \cdot \text{Sal} -0.245 \text{ pH} \cdot \text{Time} -0.245 \text{ pH} \cdot \text{Time} -0.231 \\ \text{ pH} \cdot \text{Temp} -0.123 \text{ pH} \cdot \text{Salinity} + 0.358 \text{ Tim} \cdot \text{Tem} \\ + 0.355 \text{ Tim} \cdot \text{Sal} -0.045 \text{ Temp} \cdot \text{Sal} (\text{R}^2 = 0.9241) \end{array} \tag{11}$

It is important to mention that adding quadratic terms of factors (pH \times pH, mass \times mass, etc...) did not improve prediction performance of Eq. 11.

Linear terms: Among tested factors, time (+0.132) and concentration (+0.112) have high and positive coefficients indicating that high sorption intensity at long contact time (240 min) and high concentration (500 mg L^{-1}). This was logical as higher retention is expected at longer contact time and higher dye initial concentration. Hence, the high retention observed for tests 8, 10, and 13 is attributed to the high content of dye and longer contact time. With lower coefficient (+0.056), salinity has moderate but positive influence on dye retention. Tests 5, 8, and 15 indicated high retention at high salinity, however, tests 9 and 11 showed the opposite trend, indicating factor interaction on uptake. Interestingly, mass, pH, and temperature all have negative influence (negative coefficients) on dye retention. It seems that pH has a strong influence on the process as indicated from tests 8, 10, and 15, with high affinities at pH 3.0. High sorption of direct dyes at acidic pH has been observed for many adsorbents, and attributed to surface protonation which attracts negatively-charged dye molecules (Mirzaei et al., 2018). The effect of temperature on dye uptake is interesting due to the inconsistent results reported in Table 1: running sorption tests at high temperature improved dye uptake only in one case (test 15), whereas in tests 9, 11, and 12 the same was not observed. This is again indicative of interaction among factors.

Interaction terms: as indicated in Eq. (11), the magnitudes of factor interaction coefficients were variable, the maximum positive interaction was between time-temperature (+0.358)

and time-salinity (+0.355). Negative interactions were reported among mass-time (-0.257), pH-time (-0.245), and pH-temperature (-0.231). For compost mass, the best interaction was with pH (mass \times pH + 0.226) indicating a high dve affinity at low pH and low or moderate compost mass, as observed in tests 8, 10, and 15 which showed high dye retention at low pH and intermediate mass. As shown in Eq. 11, mass and time factors have negative interaction term (mass \times time -0.257), so they should be maintained at their opposite limits to get high dye uptake. Tests 8 and 10 were operated at long contact time (240 min) and moderate mass dosage (0.40-0.60 g) and produced high dye removal (68.7–91.3 mg g^{-1}). The low coefficient for interaction between mass and salinity (-0.041) indicated the poor interaction among them, so dve sorption will not significantly affected if tests operated at the upper, lower or oppose limits of mass and salinity. Regarding concentration, the maximum interaction was reported with salinity (concentration \times salinity + 0.167) revealing that both factors should be maintained at their higher limits (tests 8 and 15). This was expected due to the aggregation of SO_3^{-1} containing-dve under the action of high salt concentrations (Sunjuk et al., 2019). The low interaction coefficient of concentration \times pH (+0.008) and concentration \times temperature (+0.089) indicated that these factors has no high synergistic influence on dye uptake. Both time and temperature should be maintained at their upper limits while keeping pH at its lower limit and test 10 is an excellent example on this situation. For contact time, the maximum interaction was observed with temperature (time \times temperature + 0.358) and salinity (time \times salinity + 0.355) demonstrating that high sorption by compost was achieved when these factors set at their upper limits as the case in test 10.

In summary, based on the results of the multilevel multifactor design, the optimum sorption conditions for DB71 uptake by the compost would be: compost mass 0.400 g, pH 3.0, temperature 50 °C, initial dye concentration 400 mg L^{-1} , salinity 0.6 M NaCl, and contact time 240 min. Thus, sorption kinetics, equilibrium sorption, and fixed-bed removal of DB71 by compost were further studied at these optimal operational conditions.

3.3. Kinetics of DB71 uptake by compost

The results of the sorption kinetics of DB71 are shown in Fig. 4 and Table 3. Kinetic analysis indicated that 28% of the maximum sorption capacity (47.6 mg g^{-1} according to the first-order kinetic model) was reached within the first 10 min of interaction. The fast uptake can be attributed to the surface chemical interaction between DB71 and composts and the contribution of film or intraparticle diffusion processes was limited. However, 200-250 min was needed to achieve equilibrium, what is in agreement with multifactorial design outputs. Model analysis indicated the superiority of firstorder model to present kinetic data (REP% 2.3) with k_1 0.054 min^{-1} and equilibrium capacity 47.6 mg g⁻¹. This suggests that DB71 interaction is achieved in a single step process. In general, first-order kinetic model do not fit well in whole range of contact time and follows in initial stage of sorption (Kushwaha et al., 2013; Anastopoulos & Kyzas, 2015). With acceptable REP% value, second-order model was also adequate to model kinetic data with $k_2 0.0014 \text{ g mg}^{-1} \text{ min}^{-1}$

and equilibrium capacity 53.6 mg g⁻¹. Moreover, this model indicated a high initial sorption rate of DB71 with a value of 4.0 mg g⁻¹ min⁻¹. Sorption rate of DB71 depends on the concentration of adsorbate at the absorbent surface and the rate controlling step involve valency forces through sharing or exchange of electrons between adsorbate and adsorbent (Kushwaha et al., 2013). The applicability of this model indicated that the overall sorption rate was controlled by chemical reaction and chemisorption significantly contribute to the entire process (Kushwaha et al., 2013). Analysis proved the limited application of internal diffusion model with REP% 12.6 and poor prediction of equilibrium capacity (11.2 mg g⁻¹).

If internal diffusion were controlling the process, then the active sites would be internally located in the porous adsorbent and the external resistance to diffusive transport process would be much lower than the internal resistance (Hamad et al., 2010). At the tested experimental conditions, kinetic-based models outperformed diffusion model, showing that dye interaction happened mainly at the surface of the compost. Some studies have discussed kinetics of DB71 uptake from solution on modified zeolite (Mirzaei et al., 2018), wheat shells (Bulut et al., 2007) and other natural minerals (Yavuz & Aydin, 2006). Compared to compost, wheat shells (with long equilibrium time 36 hr) showed relatively slower sorption rates $(k_1$ 0,002 min⁻¹, k_2 0.001 g mg⁻¹ min⁻¹, initial sorption rate 0.01 mg g⁻¹ min⁻¹ estimated at 100 mg L⁻¹, L/S 100 mL g⁻¹, pH 6.0 and 40 °C) (Bulut et al., 2007). Modified zeolite showed a moderate sorption rate for DB71 (100 mg L^{-1} , L/S 20 mL g⁻¹ 25 °C, time 120 min) with k_1 0.044 min⁻¹ and initial sorption rate 0.4 mg g^{-1} min⁻¹ (Mirzaei et al., 2018). However, sorption of DB71 by mixed silica-alumina oxide was high with k_2 0.027 g mg⁻¹ min⁻¹ measured at L/S ratio of 1000 mL g⁻¹, 30 mg L^{-1} , and 25 °C (Wawrzkiewicz et al., 2015). In any case, comparing results by different materials must be made with caution due to variations in experimental conditions or not being fully mentioned by the authors.

3.4. Equilibrium sorption and modelling

The results of the DB71 equilibrium sorption isotherm, obtained at the optimal retention conditions, along with model parameters are presented in Fig. 5 and Table 4. As shown in



Fig. 4 Kinetic profile of DB71 sorption at the optimum interaction conditions predicted by multi-factorial design. Concentration 150 mg/L, solid/liquid ratio 0.400 g/150 mL, pH 3.0 (\pm 0.3), temperature 50.0 °C (\pm 1.2).

Pseudo-first-order			Pseudo-second-order				Intraparticle diffusion			
$k_I \min^{-1}$	$q_e^{a} \mathrm{mg g}^{-1}$	REP%	k_2 g mg ⁻¹ min ⁻¹	$q_e \mathrm{~mg~g}^{-1}$	$h^{\mathrm{b}} \mathrm{mg} \mathrm{g}^{-1} \mathrm{min}^{-1}$	REP%	$k_d \operatorname{mg} \mathrm{g}^{-1} \min^{-1/2}$	$C mg g^{-1}$	REP%	
0.054	47.6	2.3	0.0014	53.6	4.0	6.8	3.11	11.2	12.6	
^a Experim	^a Experimental equilibrium capacity 49.6 mg/g.									

Table 3 Parameters of kinetic models used to present DB71 sorption by compost

^b Initial sorption rate = $k_2 q_e^2$.

Fig. 5, DB71 sorption curve presented a L2-shape according to Giles and Smith classification (Al-Ghouti et al., 2016), indicating that sorption of DB71 happens by forming a single molecular layer, with high affinity between DB71 and compost at lower concentrations and a saturation at high dye concentrations. Moreover, L2-isotherm corresponds to monofunctional adsorbate strongly attracted to a sorbent, mostly by electrostatic or ion–ion interactions, reaching saturation in an isotherm plateau (Argun et al., 2009). The same has been observed for DB71 sorption by wheat shells, activated carbon, kaolinite and montmorillonite (Yavuz & Aydin, 2006; Bulut et al., 2007; Mirzaei et al., 2018). The high L/S ratios are very promising considering the low cost of tested compost (0.5 \$ kg⁻¹) compared to other sorbents.

The interaction mechanism of DB71 uptake was further investigated by modelling sorption data using two and threeparameter models (Kushwaha et al., 2013; Ayawei et al., 2017; Al-Ghouti & Daana, 2020). The tested models have been used for presenting mono-and multilayer sorption systems.

Langmuir and Freundlich: Two-parameter isotherms. Langmuir isotherm assumes ideal monolayer sorption by a homogenous surface of equal-energy active sites (Al-Ghouti & Daana, 2020). In turn, the Freundlich model describes the reversible and non-ideal sorption on heterogeneous surfaces (Kushwaha et al., 2013). The heterogeneity arises from the presence of different functional groups on the surface of compost (as confirmed by FTIR, Fig. 2A) and the various adsorbent-adsorbate interactions. Unlike Langmuir, Freundlich model is not restricted to the monolayer formation and sorption affinities do not need to be uniformly distributed on the heterogeneous surface, so application to multilayer adsorption is possible (Issa et al., 2014). As shown in Table 4, the degree of



Fig. 5 Sorption isotherm of DB71 by compost at the optimum interaction conditions predicted by multi-factorial design. Concentration 5.0–400.0 mg/L, solid/liquid ratio 0.40 g/150 mL, pH $3.0 (\pm 0.3)$, temperature 50 °C (± 1.2), and agitation time 240 min.

fitness (REP% 6.3) indicated the better applicability of Langmuir model compared to Freundlich and Elovich models (REP % > 10), also confirming the formation of monolayer of DB71 molecules on the compost. The maximum uptake of DB71 predicted by Langmuir model was 103.8 mg g⁻¹ and slightly overestimated the experimental one (95 mg g⁻¹, Fig. 5). The estimated separation factor ($R_L = 1/(1 + K_L C_o)$ of Langmuir model indicated the favourable interaction as the value was over the range 0 < R_L < 1 (Al-Ghouti & Daana, 2020).

Sips isotherms. Sips three-parameter model is similar to Freundlich but has a finite limit at sufficiently high solute concentration. At low solute level, Sips isotherm effectively reduces to Freundlich isotherm while at high level the model predicts more realistic saturation value (Ayawei et al., 2017). The Sips model was the best among the tested models to fit sorption data (REP% 3.9) and predicted a saturation value (95.4 mg g⁻¹) very close to the experimental one. Langmuir and Sips models predicted comparable energy parameter (0.075–0.079) for DB71 sorption by compost, which indicated the presence of large enough equal-energy active sites involved in dye retention. In general, three-parameter isotherms outperformed two-parameter ones, reflecting the complexity of compost surface and presence of unequal-energy active sites.

3.5. Sorption affinity of different adsorbents

For comparison purposes, sorption affinity of local compost was compared to a Spanish compost derived from municipal solid waste MSWC, known of its high affinity for a similar dye, Direct Blue 151 (Al-Zawahreh et al., 2021). The sorption tests were carried out as outlined earlier and at 1.0 M NaCl

 Table 4
 Sorption parameters of two and three-parameter

models.						
		Parameters	Value			
Two-Parameter Isotherm	Langmuir	Q_L K_L	103.8 0.075			
	Freundlich	REP% K_F $1/n_F$ REP%	6.3 14.21 0.42 14.3			
Three-Parameter Isotherm	Sips	Q_S K_S n_S REP%	95.4 0.079 0.87 3.9			

 Q_L : Langmuir maximum capacity (mg g⁻¹); K_L : Langmuir constant (L mg⁻¹); K_F . Freundlich constant (L g⁻¹); n_F . Freundlich coefficient: Q_s . Sips saturation value (mg g⁻¹); K_s . Sips model constant; n_s . Sips model exponent.

and pH 3.0. Maximum sorption capacity for DB71 were 95.4 and 123.6 mg g^{-1} for local and Spanish compost, respectively, whereas for more DB151 these were 55.9 and 71.2 mg g^{-1} for local and Spanish composts, respectively. Thus, sorption affinity of local compost for direct dyes DB71 and DB151 is promising when compared with commercialised Spanish compost (Al-Zawahreh et al., 2021) or other materials including carbon nanotubes (4.0 mg g⁻¹, Fard et al., 2018), modified zeolite (14.0 mg g⁻¹, Mirzaei et al., 2018), kaolinite (22.0 mg g⁻¹, Yavuz & Aydin, 2006), hazelnut-derivedcarbon (26.0 mg g^{-1} , Yavuz & Aydin, 2006), wheat shells (46.0 mg g⁻¹, Bulut et al., 2007), mixed silica–alumina oxide (49.2 mg g⁻¹, Wawrzkiewicz et al., 2015), montmorillonite (48.0 mg g⁻¹, Yavuz & Aydin, 2006) and commercial activated carbon (100.0 mg g^{-1} , Yavuz & Aydin, 2006).

3.6. Dye retention in fixed-bed column

Breakthrough curves displaying $C_{\text{effluent}}/C_{\text{influent}}$ versus treated volume V or service time t are presented in Fig. 6, with the saturation values of the fix-bed adsorber estimated under differ-

1.2





Fig. 6 Breakthrough curve of DB71 sorption by compost at influent concentrations. Mass 5.00 g, bed-depth 8.8 cm, pH 3.0 (± 0.3) , 0.6 M NaCl, flow rate 1.5 mL/min.

ent dynamic experimental conditions (Eq. (12)) provided in Table 5. Fig. 6 shows typical breakthrough curves where the column capacity is fully utilized at different influent concentration of DB71. In column sorption tests, the sorbent material is practically saturated when $C_{\text{effluent}}/C_{\text{influent}}$ is 0.90–0.95 (Al-Degs et al., 2009). Analysis of breakthrough curves in Fig. 6 indicates that saturation values were 14.2, 16.7, and 17.3 mg g^{-1} for influent dye concentrations of 10.0, 15.0, and 20 mg L^{-1} , respectively. At earlier breakthrough $(C_{\text{effluent}}/C_{\text{influent}} 0.1 \text{ or}$ 1% exhaustion), the treated volumes were 1.6, 2.0 and 3.8 L for inlet dye concentrations of 10.0, 15.0, and 20 mg L^{-1} respectively. Hence, better performance was achieved at lower dye concentration. In addition, Table 5 shows saturation values (q_{column}) estimated under different dynamic conditions. The dye DB71 would be removed up to 19.6 mg g^{-1} , representing 21% of the maximum capacity of the adsorbent (95.4 mg g^{-1}), at the best retention conditions in the column: 15.0 mg L^{-1} , 1.0 mL min⁻¹, and 5.0 g packing. As shown in Table 5, lower uptakes (11.6–14.2 mg g^{-1}) were obtained at low dye influent (10.0 mg L^{-1}), low mass or short bed depth (3.0 g/5.1 cm depth), and high flow rate $(2.0 \text{ mL min}^{-1})$. The effect of bed depth on dye uptake was tested at 5.1, 8.8, and 12.8 cm: dye retention increased from 11.6 to 16.7 mg g^{-1} when bed depth increased from 5.1 to 12.8 cm (Table 5) due to higher surface area at higher bed depth (Han et al., 2007). However, sorption performance of compost was slightly reduced when increasing packing to 7 g. Hence, 5.0 g (8.8 cm bed depth) was selected as the optimum packing. Moreover, flow rate is also an influential parameter for DB71 retention in bed adsorber (Han et al., 2007). When flow rate was reduced from 2.0 to 1.0 mL min⁻¹ while keeping packing and initial concentration at 5.0 g and 15.0 mg L^{-1} , respectively (tests 2, 6, and 7), DB151 sorption increased from 12.5 to 19.6 mg g^{-1} . This observation was attributed to increasing contact time between dye solution and particles of compost at lower flow rate leading to better interaction (Akar et al., 2014).

3.7. Recycling of dye-loaded compost

Reversibility (dye elution by water) and desorption (dye elution with solvents other than water) of DB71 was investigated to assess the recycling potential of the exhausted compost (Kumar & Ahmad, 2011; El-Barghouthi et al., 2007). The proper selection of a solvent for desorption is a significant

Table 5	Maximum uptake of DB/I estimated at different dynamic conditions.								
Test	C_o (mg L ⁻¹)	Flow rate (mL min ⁻¹)	Mass (g)	Bed depth cm	$C_{effluent}$ at $\approx 95\%$ saturation	$q_{column} \ ({ m mg \ g}^{-1})^{ m a}$	$(q_{column} \ q_{max}) imes 100^{ m b}$		
1	10.0	1.5	5.0	8.8	9.5	14.2	15		
2	15.0	1.5	5.0	8.8	14.6	16.7	18		
3	20.0	1.5	5.0	8.8	19.1	17.3	18		
4	15.0	1.5	3.0	5.1	14.4	11.6	12		
5	15.0	1.5	7.0	12.8	14.6	15.6	16		
6	15.0	1.0	5.0	8.8	14.5	19.6	21		
7	15.0	2.0	5.0	8.8	14.3	12.5	13		

^apH 3.0, salinity 0.6 M NaCl, and 25 °C (\pm 1.2).

^cUtilization of ultimate equilibrium capacity ($Q_{\text{max}} = 95 \text{ mg/g}$, Fig. 5).

^b Column capacity estimated at 95% saturation ($C_{\text{effluent}} \approx 0.9 C_{\text{influent}}$) from Eq. (12).

Table 6 Recycling of DB71 using different solvents. ^a											
Cycle	Solvent ^b	Solvent ^b									
	0.1 M HNO ₃	<i>n</i> -Hexane	H ₂ O	0.1 M NaOH	Ethanol						
1	6.6	8.8	15.4	17.6	39.6						
2	4.6	4.0	8.8	11.0	15.4						
3	2.2	4.4	4.4	6.6	6.6						
Total % Desorption	13.4	17.2	28.6	35.2	61.7						

^a The reported percentages were taken as an average of three identical desorption tests (n = 3, RSD < 8.1).

^b Desorption by water was performed at the conditions (pH 3.0, 0.6 M NaCl, and 50 °C) while by other solvents at 25 °C and without adjusting pH or adding salt.

issue and depends on the structure of compost and sorption mechanism (Vijayaraghavan et al., 2008). The results of DB71 desorption by different solvents are provided in Table 6. Only 28.6% of the adsorbed dye was removed by water indicating the irreversible nature of the process, as a large fraction (71.4%) of DB71 remains strongly retained by the compost. Low desorption rate by HNO₃ was expected as the highest sorption was achieved at pH 3.0, so increasing acidity was not helpful to elute dye. On the other side, increase in dye desorption by NaOH responds to the higher solubility of reactive dyes in basic solution or break down of dye-compost forces formed under acidic conditions. In general, dye desorption using aqueous solvents (H₂O, 0.1 M HNO₃, 0.1 M NaOH) was low (13-35%) indicating the chemisorption nature of the interaction. Diverse results were observed for organic solvents: *n*-hexane presented a very low desorption rate (17.2%) while ethanol presented the highest efficiency (61.7%). This is likely due to high polarity compared to *n*-hexane. The weak capacity of *n*-hexane to elute dye may impair the participation of hydrophobic-hydrophobic in DB71 uptake by compost.

3.8. Mechanism of interaction

At the tested pH range (3.0–9.0), both compost and DB71 can ionize in solution with possible interaction via electrostatic and salt-bridge forces. Moreover, polar-polar and hydrophobichydrophobic interactions are also possible. As indicated from multilevel multifactor design, the maximum dye retention was observed at acidic solution (pH 3.0), high salinity (0.6 M NaCl), and high temperature (50 °C). At pH 3.0, significant electrostatic attraction can happing as dye (pH_{solution} > pK_a) and compost (pH_{ZPC} < pH_{solution}) present electric charges of opposite sign. In this sense, better removal of DB71 in acidic medium has been also reported for modified zeolite (Mirzaei et al., 2018). The higher affinity observed in saline solution can be due to two factors: a) the salting-out effect, in which dye solubility decreases, resulting in more migration to the surface, and b) dye aggregation caused by salt, resulting in more surface attachment. In fact, salt has been shown to have a beneficial effect on the aggregation and uptake of SO_3^- containing dyes (Sunjuk et al., 2019; Al-Degs et al., 2008).

The nature of the interaction mechanism can be further studied by examining FTIR spectra. DB71 has three azo bonds N = N, four ionizable sulfonate groups, polar functional groups (N-H and O-H), and a massive hydrophobic skeleton made up of four naphthalene molecules, as illustrated in Fig. 1. The FT-IR spectra of dye-loaded compost (Fig. 2)

revealed many peaks in the range about 700 and 1000 cm^{-1} . which are often linked with the out-of-plane bending bands of substituted benzenes. The complexity of dye interaction mechanism is observed in the band at 1029 cm⁻¹ (which accounts for C-OH bond stretching), as its intensity was notably improved after dye interaction reflecting the contribution of H-bonding in the process. As shown in Fig. 2, dye sorption increased intensity of the peaks at 2916 and 2862 cm^{-1} (which correspond to C-H band stretching), supporting the contribution of hydrophobic interaction between compost and DB71. The characteristic band of azo bond at 1400–1500 cm^{-1} (Hu et al., 2003) increased in the dye-loaded-compost, indicating the presence of DB71 on the surface. Meanwhile, the band at 1623 cm⁻¹, which corresponded to the C-C and C = C of mature humic acid, was displaced to 1650 cm^{-1} , indicating that hydrophobic forces played a role in the process. The higher intensity of 873 cm⁻¹ (due to C-H bond waging) after dye sorption also points in the same direction, so in summary, FTIR analysis supports the contribution of hydrophobichydrophobic interaction mechanism to dye removal.

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4. Conclusions

Use of waste materials, such as composts, as low cost adsorbents for dye removal from wastewater is recently gaining increasing attention. In this work, the affinity of a food waste compost for removing weakly interacting Direct Blue 71 from solution was evaluated. The influence of six operational factors on dye uptake by this compost was assessed for the first time using a multilevel multifactor design. Analysis of sorption data indicated high linear effects of concentration (+0.122) and contact time (+0.132) on dye uptake while mass/pH/temperature have insignificant influence. The study also confirmed positive interactions between time and temperature (+0.358), time and salinity (+0.355), sorbent mass and pH (+0.226), concentration and salinity (+0.167); as well as negative interactions between sorbent mass and time (-0.257), and pH and temperature (-0.231). The outputs of multifactor design allowed to determine the optimum combination of experimental factors: sorbent mass 0.40 g, pH 3.0, initial dye concentration 400 mg L⁻¹, contact time 240 min, salinity 0.6 M NaCl, and temperature 50 °C. The three-parameter Sips sorption model explained better the observed sorption data in comparison to two-parameter models (like Freundlich), reflecting the complexity and diversity of the surfaces of composts and the presence of different active sites. Analysis of FTIR spectra after dye sorption would evidence the contribution of hydrophobichydrophobic forces in the sorption process.

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CRediT authorship contribution statement

Khaled Al-Zawahreh: Methodology, Validation, Writing – review & editing. Yahya Al-Degs: Conceptualization, Methodology, Validation, Writing – review & editing. María Teresa Barral: Conceptualization, Writing – review & editing. Remigio Paradelo: Conceptualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author (Yahya Al-Degs) on reasonable request.

Appendix 1. Significance *t*-test for the importance of estimated terms in Eq. (13)

Term		Coefficient	v	t
Linear	Mass	-0.050	40.2	0.00061
	Conc	0.112	28.9	0.00159
	Ph	-0.014	30.7	0.00019
	Time	0.132	33.7	0.00175
	Temp	-0.074	28.4	0.00106
	Sal	0.056	38.1	0.00069
Interaction	$Mass \times Conc$	0.103	29.4	0.00146
	$Mass \times pH$	0.226	26.4	0.00338
	$Mass \times Time$	-0.257	25.8	0.00389
	$Mass \times Temp$	-0.112	29.6	0.00158
	$Mass \times Sal$	-0.041	35.8	0.00053
	$Conc \times pH$	0.008	33.4	0.00010
	$Conc \times Time$	0.100	31.7	0.00136

Annendix	1.	(continued)
1 ipponding		(continuction)

Term		Coefficient	v	t
	$Conc\timesTemp$	0.089	32.7	0.00119
	$Conc \times Sal$	0.167	36.1	0.00214
	$pH \times Time$	-0.245	30.3	0.00341
	$pH \times Temp$	-0.231	30.8	0.00319
	$pH \times Sal$	-0.123	34.4	0.00161
	Time \times Temp	0.358	31.4	0.00489
	Time \times Sal	0.355	30.2	0.00496
	$Temp \times Sal$	-0.045	33.2	0.00060

 $S_E = 173$, s = 17.3, df = N-P = 10, t_{table} at 90% confidence level 1.81.

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