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Biosorption of bemacid red dye by brewery waste using single and poly-parametric study

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ABSTRACT

Brewery waste is used as a low-cost adsorbent to remove the BemacidRed dye. Effect of parameters: pH solution, initial dye concentration, adsorbent mass and contact time on the dye removal are determined by single parametric kinetic study. Two type forms of equilibrium isotherm are tested Langmuir and Freundlich models. The best fit of equilibrium data with maximum amount removal of 142 mg/g (pH = 2, contact time = 60 min, adsorbent mass = 50 mg) is provided by Langmuir isotherm. The poly-parametric study using the complete factorial design approach is performed. Residual analysis was used to confirm the validity of the linear model with first order interaction obtained by the poly-parametric method. It was observed that the initial pH have an important negative effect equal to –14 on Bemacid Red dye elimination. In contrast, the initial dye concentration has positive effect equal to +11. Furthermore, the results of the poly-parametric study are consistent and significant compared to the results of single-parametric study with a reduced number of experiments. These conclusions available to consider that the brewery waste can be successfully applied for the Bemacid Red dye removal.

Keywords: Bemacid Red dye; Brewery waste biosorption; Full factorial design; Isotherm

1. Introduction

The use of various forms of organic pollutants, as dyes, in the industries (textile, tannery, painting...) contributed negatively in the environment pollution [1,2]. In order to solve these problems, different research studies are based on the elimination or reduction of organic pollutants from wastewater by conventional physicochemical and biological methods [3,4]. Among these methods, the adsorption which is physicochemical elimination is a simple and effective method. In order to select the low-cost adsorbent, a variety of biomass are used in adsorption phenomena, such as olive stones [5], date stones [6], apple pulp [7], *Arundodonax* [8], banana peel [9]. Removal efficiency of the low-cost adsorbent is related to a large number of operating parameters, such as pH of solution, initial pollutant concentration, and adsorbent mass [10–12]. To optimize the effect of these parameters towards the pollutant uptake, single parametric method is used. It is classic method which consists to varying one factor and maintaining others at constant values is used. This method is repeated according to the number of parameters and their values with drawbacks which are consumption of time and material [13,14]. To reduce these drawbacks, another optimization method is chosen; it is about the poly-parametric study. It gives important information on all necessary number of experiences, on the effect of interaction of the parameters into the removal amount, on adequate of the mathematical model with the data [15–17]. It consists to plan the experiments using any model of factorial experimental design or response surface methodology approach [15]. Moreover, these methods allowed to vary all the variables from one experiment to the next, and are widely employed to estimate the individual effects and the interaction effects between the parameters, giving a valid conclusion regarding to the optimization [16].

The present work aims to study the impact of four process parameters (pH solution, initial solution con-

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centration, adsorbent mass and contact time) on the adsorbed amount of Bemacid Red dye from an aqueous solution using brewery waste as adsorbent with a single parametric study. To screen the factors (parameters) and their interactions, as well as the adsorption conditions optimization, the full factorial design is performed as poly-parametric study.

2. Materials and methods

2.1. Adsorbent and adsorbate

Spent grain was obtained as an industrial waste from Oran breweries (west of Algeria). Samples were washed several times using distilled water to remove impurities. The biomass was then dried in oven at 80°C during 48 h. The dried biomass was ground to a fine powder, sieved to obtain average sizes (250 µm).

Bemacid Red (B-R) dye which belongs to the family of Bemacid-ETL dyes with unknown structure is obtained from SOITEX textileplant, Tlemcen (west of Algeria). The working stock solution was prepared by dissolving 1 g of B-R in distilled water. To test the adsorption; the desired concentration of working solutions are prepared by diluting the stock solution.

The pH of the dye solution was adjusted by adding NaOH (0.1 or 0.01 M) or HNO_3 (0.1 or 0.01 M), using pH-meter (SCHOTT CG711).

The point of zero charge was estimated according to the method described by Maliheh et al. [18]. FTIR analysis was used to identify the characteristic functional groups on the surface of the adsorbent. The structure and morphology of spent grain were characterized by transmission electron microscopy (SEM).

2.2. Experimental methods

Adsorption of B-R was studied in batch mode which is single parametric study. For this, 50 mg of brewery waste was placed in conical flasks with 50 mL of B-R dye at 25 mg/L at room temperature (24–25°C). Effect of several parameters is studied, pH solution between 2 and 9, initial dye concentration between 5 and 800 mg/L, adsorbent mass 50, 75 and 100 mg contact and time between 5 and 60 min. The mixtures were stirred at 300 rpm. The equilibrium concentrations of the solutions were determined using UV-Vis spectrophotometer (HACH DR 2000) at 500 nm.

The percentage removal (R %) and the quantity adsorbed q_e (mg/g) of B-R on brewery waste were calculated using the following equations [19–20]:

$$R\% = \frac{C_0 - C_e \cdot 100}{C_0} \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (2)$$

where C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of B-R dye at time t respectively, m (g) is the mass of biomass and V (L) is the volume of samples dye solution.

3. Results and discussions

3.1. Brewery waste characterization

In order to identify the functional groups responsible for B-R dye removal, the FTIR spectrum of brewery waste was evaluated (Fig. 1). Brewery waste is lignocelluloses biomass. The broad band at 3421 cm^{-1} corresponds to the O–H bond of elongation vibration [21]. The asymmetric and symmetric vibration bands C–H of cellulose are locates at 2929 and 2870 cm^{-1} respectively [22]. The peak around 1747 cm^{-1} is characteristic of the stretching vibration of C=O of the carboxylic acids of hemicelluloses present in the biomass [21]. The tow band 1655 and 1549 cm^{-1} are attributed to the deformation of C=C aromatic of lignin [6]. The vibration of methoxygroups of lignin C–O observed at the peak of 1248 cm^{-1} [6]. The peak at 1045 cm^{-1} corresponds to the C–OH elongation vibration [22]. The image obtained by SEM (Fig. 2) indicates that the morphological surface of the adsorbent has a homogeneous and porous structure.

3.2. Adsorbent pH_{pzc}

The pH_{pzc} of the adsorbent is an important factor in understanding the adsorption process. The pH drift method was used, and the intersection of both curves of the initial and final pH was pH_{pzc} (Fig. 3) [18]. This parameter was

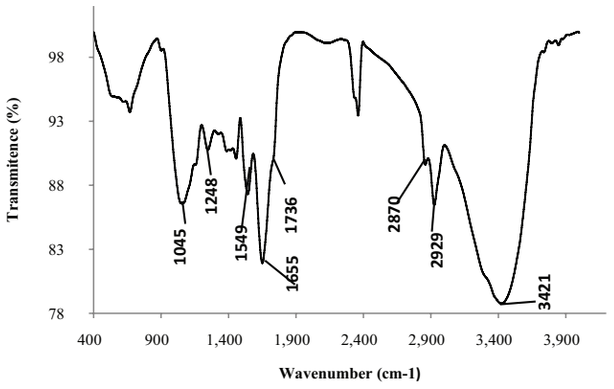


Fig. 1. FTIR Spectra of brewery waste.

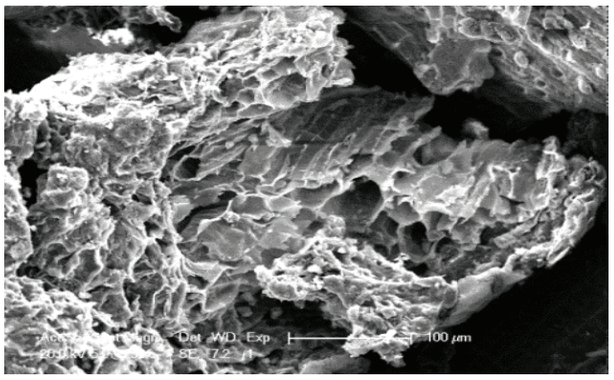


Fig. 2. SEM of brewery waste.

found be equal to 6.1; that means in acid medium (pH < pH_{pzc}) the surface of adsorbent becomes positively charged, which helps to eliminate basic dyes and at basic medium (pH > pH_{pzc}) the surface of adsorbent becomes negatively charged which eliminate acidic dyes. The determination of pH_{pzc} was used for different biomass as the white pine sawdust was found to be equal to 4.25 [23].

3.3. Results of single-parametric study

3.3.1. Effect of pH on B-R dye removal

As shown in Fig. 4, the B-R amount adsorbed increase from 7 to 43; 3 to 31 and 1 to 20 mg/g when the pH of the solution decrease from 6 to 2 for 100, 63 and 25 mg/L of initial B-R concentration respectively. So, it is easy to perceiving that the B-R removal was favorable in acidic condition. The BR belongs to the Bemacid-ETL family which has an anionic auxochrome group, which explains the efficiency of BR dye removal in acidic medium. In effect, at pH solution < pH_{pzc} of adsorbent, the surface of adsorbent is positively charged that'll scream the attractions forces between positive sites of adsorbent and those negative of B-R dye. The same observations and conclusions are reported by other authors [24,25]. The results obtained indicate that the pH plays an important role in the B-R dye adsorption

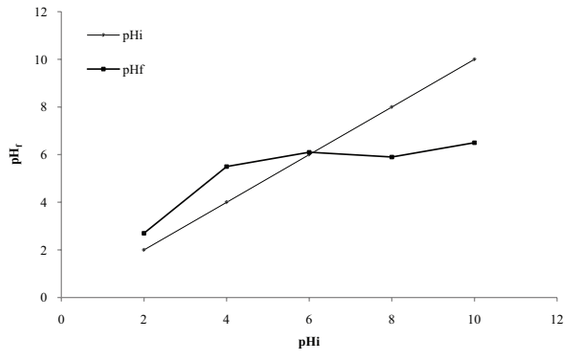


Fig. 3. pH_{pcz} of spent grain.

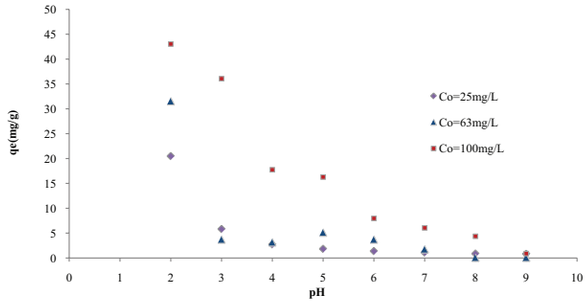


Fig. 4. Effect of initial pH on the removal of the BR dye at different initial B-R concentration.

3.3.2. Effect of spent grain mass and contact time on B-R removal:

As shown in Fig. 5, the biosorption process begins with a very fast step during the first five minutes in all cases (a, b and c). After this, the biosorption slightly increased up to 20 min. Thereafter, the amount of removal was fixed within 40 min; this time is the reached equilibrium biosorption, this area of the graph means that all adsorption sites are saturated by the dye. Concerning the sorbent dosage effect, the amount of dye biosorbed per unit mass of biosorbent decreases from 20 to 12 mg/g for initial B-R concentration of 25 mg/L with an increase in mass biosorbent from 50 to 100 mg (Fig. 5a). This can be explained by the fact that the collision and aggregation of biosorbent causes the decrease in the total area available that leads to a reduction of elimination [25]. In all cases, the minimum effective adsorbent improves the adsorption capacities. The same results were also observed by the adsorption of textile dyes onto wheat straw and apple pomace [26] and cross-linked chitosan [27].

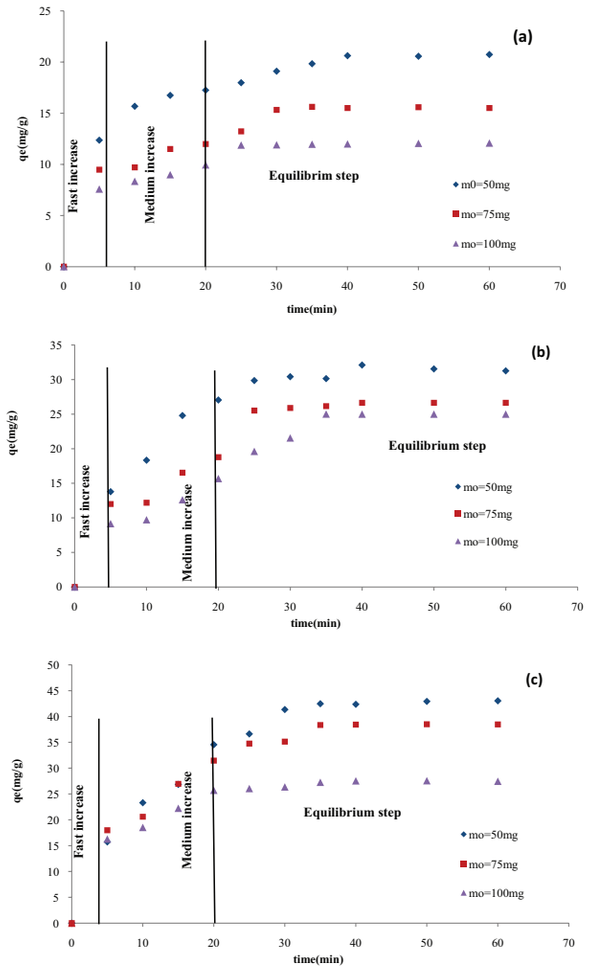


Fig. 5. Effect of biomass mass on B-R removal at different initial B-R concentration: (a) 25 mg/L (b) 63 mg/L and (c) 100 mg/L.

3.3.3. Effect of B-R dye initial concentration on B-R removal

The impact of initial dye concentration on the brewery waste efficiency can be seen from Fig. 6. The amount of dye biosorbed increased when the initial B-R concentration increase. This may be due to the increase of B-R ions number around adsorbent sites which became much more [28,29]. In addition to that, an important driving forces to control all mass transfer resistances of the dye between the aqueous and solid phases is provided by a high initial concentration, thus increases the uptake [30,31]. The experimental maximum adsorbed amount of 142 mg/g is observed at initial dye concentration of 400 mg/L for the minimum mass adsorbent m = 50 mg which is in agreement with the results obtained in the effect of adsorbent mass study.

3.3.4 Kinetic study:

The biosorption mechanism of any pollutants elimination from an aqueous solution by any adsorbent can be described by using kinetic models and by analyzing the rate controlling the pollutant removal [32]. The following equations (pseudo-first order, Eq. (3); pseudo-second order, Eq. (4)) [32] were selected to appropriate the experimental kinetic data.

$$\log\left(q_e - q_t\right) = \log q_e - k_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where q_e and q_t correspond to the amount adsorbed per unit mass of adsorbent (mg/g) at equilibrium and at time t, respectively, k_1 and k_2 corresponds to the rate constant for first and second-order kinetics.

Both models are illustrated in Figs. 7 and 8 for the different mass adsorbent and different initial dye concentration. The determination and comparison of the regression coefficients R^2 and the value of the calculated adsorbed amount indicate the conformity between experimental data and the kinetic model.

The linearity of the plots demonstrates that the pseudo-first order kinetic models do not play a notification role in the adsorption of the B-R dye by brewery waste in the case of Fig. 7a, 7b and 7c. There is no conformity between the values of the experimental and calculated adsorbed amount, except for the mass adsorbent m = 75 mg, where the model fitted well the data at different initial dye concentration. In this case, the values of calculated adsorbed amount are similar to experimental ones, q_{exp} = 15 mg/g and q_{cal} =15.66 mg/g, q_{exp} = 26 mg/g and q_{cal} = 25.58 mg/g and q_{exp} = 38 mg/g and q_{cal} = 34 mg/g for 25 mg/L, 63 mg/L and 100 mg/L respectively. Also, in the case of adsorbent mass m = 100 mg and initial dye concentration C_0 = 63 mg/L, for Table 1 is well represented by the pseudo-first order kinetic model.

For the remaining cases, the dyes removal kinetics can be considered as pseudo-second order through the linear fit between the t/q_t versus operating time (t) and calculated regression coefficients (Table 2). In addition, the experimental q_{exp} values are similar with the calculated ones, obtained from the linear plots of pseudo-second order kinetics (Figs. 8a–c).

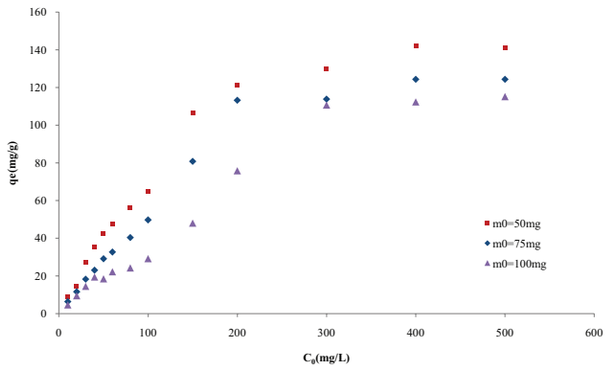


Fig. 6. Effect of initial B-R concentration on B-R removal.

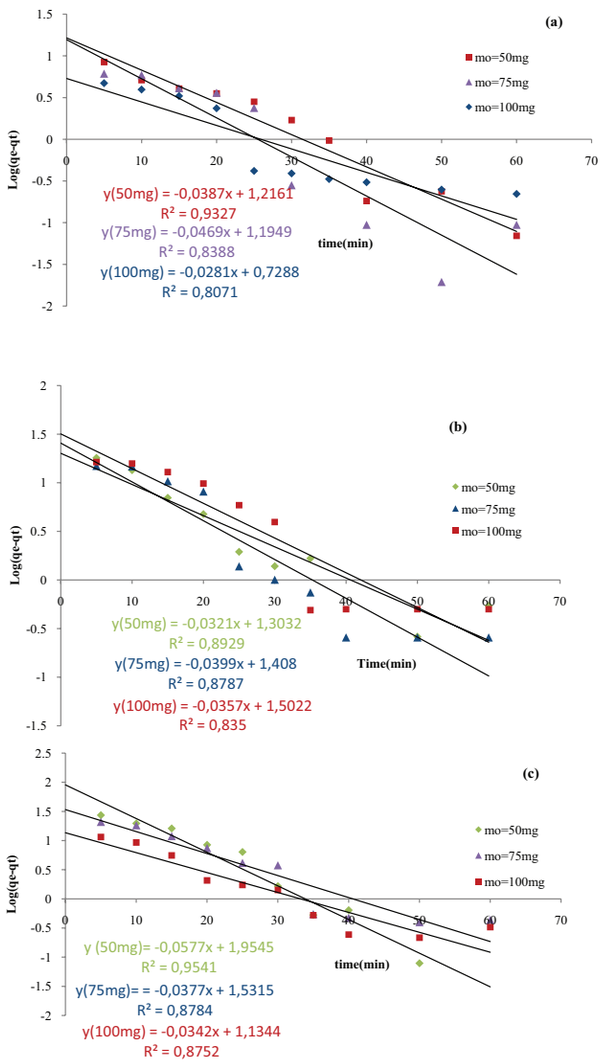


Fig. 7. Pseudo-first order plot for the adsorption of B-R on brewery waste: (a) 25 mg/L (b) 63 mg/L and (c) 100 mg/L.

Table 1
Kinetic parameter of pseudo first and second order models

B-R concentration	25 mg/L			63 mg/L			100 mg/L		
Biomass weight, mg	50	75	100	50	75	100	50	75	100
q_e (experimental) mg/g	20	15	12	31	26	23	43	38	27
Pseudo first order									
K_1 (min^{-1})	0.037	0.046	0.028	0.032	0.022	0.035	0.057	0.037	0.034
q_{cal} ($mg \cdot g^{-1}$)	16.44	15.66	5.24	20	25.58	31.7	90	34	13.6
R^2	0.93	0.83	0.8	0.89	0.87	0.83	0.95	0.87	0.87
Pseudo second order									
K_2 (g mg^{-1} min^{-1})	0.008	0.008	0.014	0.003	0.004	0.005	0.001	0.002	0.007
q_{cal} ($mg \cdot g^{-1}$)	22.52	17.6	13.33	36	33	35	53.4	45.6	30.1
R^2	0.99	0.98	0.99	0.99	0.96	0.99	0.98	0.99	0.99

Table 2
Equilibrium parameters for the adsorption of ETL dye onto brewery waste biomass at optimum pH

Adsorbent mass(mg)	50	75	100
Freundlich			
n	2.1	1.9	2.7
K_f	13	12.2	10.1
R^2	0.84	0.91	0.86
Langmuir			
q_m (mg/g)	142	142	142
K_L	0.04	0.03	0.02
R_L	0.05	0.07	0.1
R^2	0.97	0.96	0.94

3.3.5. Biosorption isotherms modeling

To give a sense of equilibrium between the B-R ions adsorbed on the surface of the spent grain and the remaining dye ions in the aqueous phase, Langmuir and Freundlich models are tested. To determinate the adsorption constants the linear mathematical expressions (5), (7) of these models are applied.

Langmuir isotherm linear form [33]

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{5}$$

The evaluation of the isotherms and their feasibility were checked by R_L factor (Eq. (6)):

$$R_L = \frac{1}{1 + K_L \cdot C_0} \tag{6}$$

The R_L value indicates the sorption mode. If the process is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$)

Freundlich isotherm linear form [34]

$$\log q_e = \ln K_f + \frac{1}{n} \log C_e \tag{7}$$

where q_e (mg/g) is the equilibrium amount dye concentration in the solid phase; q_m (mg/g) is the maximum amount of adsorption; K_L (L/mg) is the Langmuir adsorption equilibrium constant representing the affinity of adsorbate to binding sites of the adsorbent; K_F is the Freundlich constant representing the adsorption capacity, n is the constant depicting the adsorption intensity.

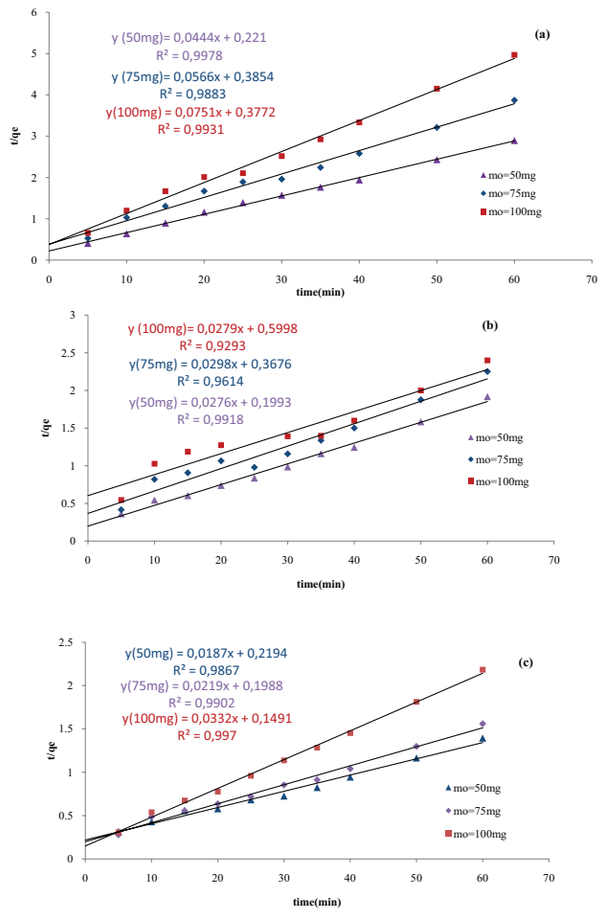


Fig. 8. Pseudo-second order plot for the adsorption of B-R on brewery waste: (a) 25 mg/L (b) 63 mg/L and (c) 100 mg/L.

The Langmuir model suggests that the adsorption is carried out in monolayer on the adsorbent which presents a homogeneous surface without interaction between the molecules of the adsorbate [33].

The maximum adsorption capacities of brewery waste and adsorption constants parameters are summarized in Table 2. The linear fit between the C_e/q_e versus C_e and calculated regression coefficients (R^2) show that the adsorption dye isotherm can be fitted well by Langmuir model in all case (Fig. 8). This means that, the adsorption is monolayer and the B-R is rearranged homogeneously on brewery waste sites. The calculated maximum adsorption capacities (q_{max}), was be found equal to 142 mg/g at pH = 2, which is higher comparing to the value of acid orange 7 dye removal by the same biomass 29 mg/g [35]. Table 3 summarizes some value of maximum biosorption capacity at ambient temperature (20–25°C) and proves that the brewery waste is more effective in ETL elimination compared with other pollutants.

Langmuir constant K_L depict the affinity of B-R to binding sites of the adsorbent [36]; is calculated as 0.02 l·mg^{-1}. In the present study, the K_L value obtained is higher than that reported by [37] who have use aniline blue biosorbed into spent grain; a high value of K_L notifies the strong binding of B-R ions to brewery waste. In all cases, the value of Freundlich constant $1/n$ was found to be less than 1, as shown in Table 2; this means that, the adsorption is favorable which is in according to Treybal [38]. Also and from Table 2, the R_L values at different initial B-R concentration are within the range 0–1 , which indicate that the adsorption of B-R on the brewery waste is favorable.

3.4. Full factorial designs optimization:

The poly parametric study using the full factorial design was used to evaluate the effect of factors (operating conditions) into the brewery waste efficiency. This approach methodology is a useful statistical tool to optimizing parameter of different processes [39,40], the response in the full factorial design signifies the rate of B-R elimination and the factors mean the operating conditions. MINITAB (17) statistical software (evaluation version) was used to reach experiments design. The design of the plan to be realized according to the full factorial model requires the application of the relation which links the number of factors to be studied and the number of experiments to be carried out. The experiments number to achieve is 2^n, where 2, indicates the two levels of factors and n is the number of factors. Four factors with two levels were employed initial pH solution (2, 4), initial dye concentration (C) (25, 100 mg/l), sorbent mass (m) (50, 100 mg) and contact time interval (t) (10, 50 min) which gives a group of experiments equal to sixteen.

Fig. 9 shows the experiment design generated by the full factorial design. A first-order model with all possible interactions between the factors was chosen to describe the experimental data. After running the model of the full factorial design the Eq. (8) gives the relationship between the removal amounts q_e and the four studied factors.

$$q_e = 13{,}213 - 7{,}413\ pH - 2{,}009\ m + 5{,}969\ C + 2{,}725\ t - 2{,}236\ pH.C - 3{,}417\ pH.t - 1{,}390\ m.C - 0{,}860\ pH.m.C + 2{,}624\ pH.m.t - 2{,}286\ pH.C.t + 1{,}335 m.C.t + 1{,}563\ pH.m.C.t \quad (8)$$

The coefficients values of the parameter in Eq.(8) indicate the quality of the effects of these factors on the removal of the dye. The validity of the results, initial dye concentration and contact time with positive effect on the B-R elimination and a negative effect for the others parameters Fig. 10; this results are valid only in the range of the values of the four factors of this present study.

This means that the sorption of B-R must be operating under the following value of the four studied factors: lowest levels of pH and mass sorbent and highest levels of the

Table 3
Langmuir based maximum biosorption capacity at ambient temperature (20–25°C)

Pollutants	q_m (mg/g)	References
Bemacid Red	142 (at T = 25°C)	This study
Acid orange 7	29 (at T = 20°C)	[35]
Cu	62.5 (at T = 25°C)	[39]
Cd	27.9 (at T = 25°C)	[40]
Basic dye Rhodamine	20.4 (at T = 25°C)	[41]
Basic Red 46	13.2 (at T = 25°C)	[42]
Basic Blue 3	12.2 (at T = 25°C)	[42]

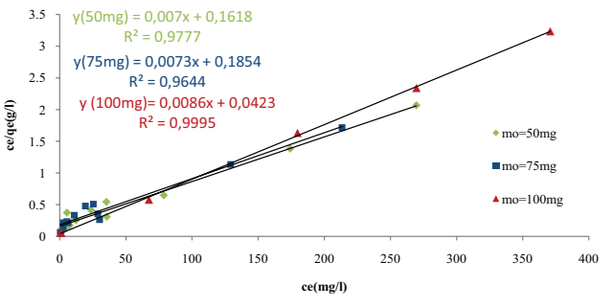


Fig. 9. Adsorption isotherms using linear form of Langmuir isotherm for ETL onto brewery waste.

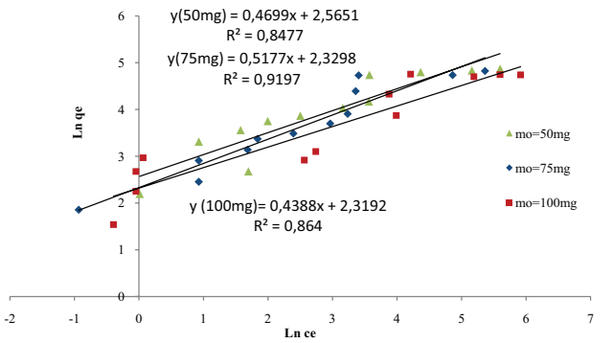


Fig. 10. Adsorption isotherms using linear form of Freundlich isotherm for ETL onto brewery waste.

initial dye concentration and contact time (−, −, +, +). Thus, the order of significant factors that affect the adsorption of the dye first finds the initial pH, followed by the initial concentration of the dye.

The t-test was using to evaluate the significance of these effects with a significance level of 5%.

The effect of parameter is significant when the value of P is lower compared to the value of significance level selected.

From Table 4, the first column represents the studied factors and their interaction, the second column represents the effect of each factor, the third column represents the coefficients of the mathematical model, the fifth column represents the values of student test t and the last column represents the values of the probability P. The variability q_e presented by the model indicate R-square statistic value of 99.85%. Also from (Table 4), the P-value defined as the lowest level of significance leading to the rejection of the null hypothesis and shows that the main effect of each factor and the interaction effect were statistically significant: $P < 0.05$ [16].

The different types of interaction between the studied variables and the optimum conditions are illustrated in the 3D surface plots (Fig. 11). ETL dye concentration and operating time have the same effect on dye removal efficiency q_e (mg/g) for brewery waste biomass. Fig. 11a, when the ETL dye concentration increase from 25 to 100 mg/L and operating time from 10 to 50 min, q_e (mg/g) takes a highest value. Fig. 11b illustrates the interactive effect of process operating contact time with sorbent dosage at constant pH = 3 and C = 63 mg/L, these parameters have an opposite effect on the response, indeed when the sorbent dose decrease and contact time increase, the response increase. The same observations on the response between biomass dose and dye concentration, pH and dye concentration and between pH and sorbent weight are made (Figs. 11c, e and f). In the case of Fig. 11d, the plot shows that when pH and sorbent dose decrease the response increase. These observations of 3D surface are in agreement with result obtained in the batch sorption.

The optimizing of the response through the full factorial model gives the following process conditions: pH = 2, initial dye concentration = 100 mg/l, sorbent mass = 50 mg and for contact time = 50 min, these conditions allow us to calculate the maximum value of q_e which is equal to q_e = 42.62 mg/g.

This approach methodology is adequate to determine the amount of B-R dye removal, and also describe the biosorption process for this pollutant and others [15,16].

Table 4
Estimated effects and coefficients for q_e (mg/g)

Term	Effect	Coeff	CoefErT	Value T	Value P
Constant		13.213	0.262	50	0.000
pH	–14.825	–7.413	0.262	–28.27	0.000
m	–4.018	–2.009	0.262	–7.66	0.005
C	11.938	5.969	0.262	22.76	0.000
t	5.450	2.725	0.262	10.36	0.002
pH. C	–4.473	–2.236	0.262	–8.53	0.003
pH. t	–6.835	–3.417	0.262	–13.03	0.001
m. C	–2.780	–1.390	0.262	–5.3	0.013
pH.m.C	–1.720	–0.860	0.262	–3.28	0.046
pH.m.t	5.247	2.624	0.262	10.01	0.002
pH.C.t	–4.572	–2.286	0.262	–8.72	0.003
m.C.t	2.670	1.335	0.262	5.09	0.015
pH.m.C.t	3.125	1.536	0.262	5.96	0.009
S		Rsqu	Rsqu (ajust)	Rsqu (est)	
1.04888		99.85%	99.25%	95.75%	

4. Conclusion

The results of this study enable to report that brewery waste sorbent have significant adsorption capacity for B-R dye comparing to others pollutants. The B-R amount uptake was found to be dependent on pH, contact time, initial dye concentration and adsorbent dose. Also, equilibrium isotherm data were best described by Langmuir isotherm model with a maximum capacity of q_e = 142 mg/g. Kinetic study obeyed pseudo-second-order model for general studied case. Based on the results, brewery waste can be potentially considered as a new raw material of low cost sorbent used for B-R uptake. Full factorial 2^4 design was used to optimizing the operating conditions. This method gives the significant effect into the B-R uptake. Also, gives the optimum factors to maximize the B-R amount removal. pH and sorbent mass have negative affect into the B-R amount uptake. However, the initial dye concentration has positive effect. This approach methodology is adequate to describe the biosorption process and to analyzing the dependence of the factors into the response.

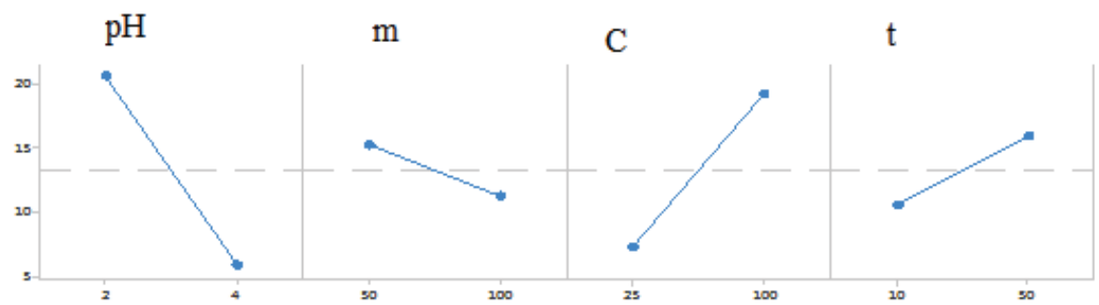
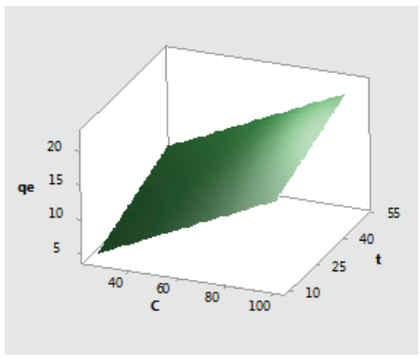
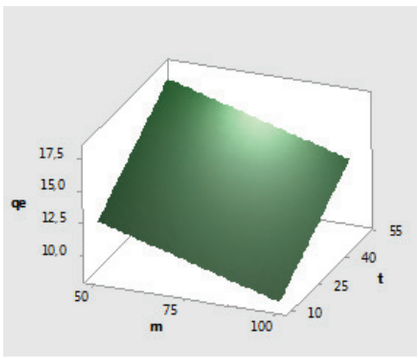


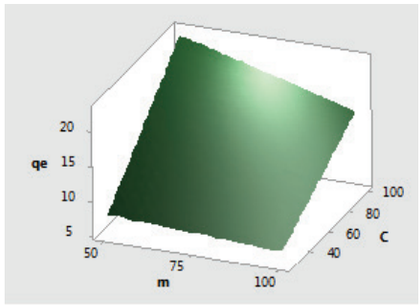
Fig. 11. Effect of studied factors.



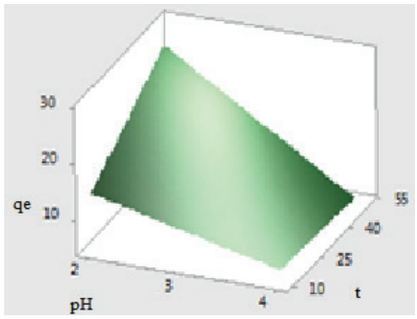
(a) pH=3 and m=75



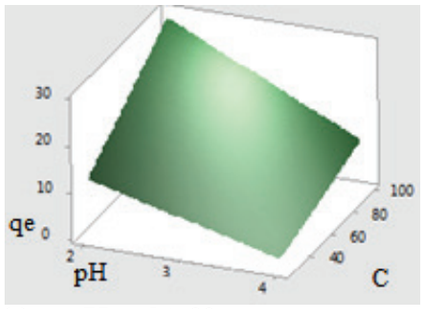
(b) pH=3 and C=63



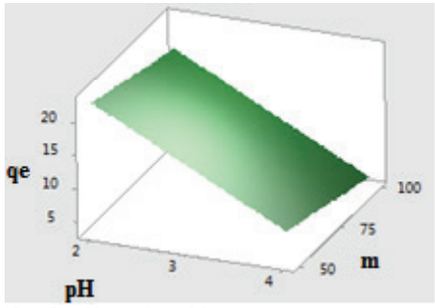
(c) pH= 3 and t=30



(d) m=75 and C=63



(e) m=75 and t=30



(f) C=63 and t=30

Fig. 12. Surface plot of the B-R removal at the center point.

Dedication

This work is dedicated to the memory of Mr., Pr. Mohand Said OUALI, from AbdelhamidIbnBadisUniversity – Process Engineering Department – Valorization of materials laboratory. Mostaganem-Algeria.

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