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Optimization and modeling of decolorization and COD reduction of reactive dye solutions by ultrasound-assisted adsorption

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Abstract

The treatments of wastewaters contained dyestuffs are difficult and they require special advanced treatment technologies. It is known that adsorption is one of the methods commonly and efficiently used for treatment of textile wastewaters. In this study, the removal of reactive dye rifacion yellow HE4R was studied by using both ultrasound and combined ultrasound/activated carbon. The effects of relevant parameters, namely; ultrasound power, temperature, time, activated carbon concentration, dye concentration and initial pH have been investigated on the decolorization and COD reduction by using the fractional factorial design and the orthogonal central composite design. A model has been obtained among decolorization, COD reduction and relevant parameters by means of variance analysis by using the matlab computer software and obtained model was optimized. 80.62% decolorization efficiency was accomplished by ultrasound. Afterwards, combined ultrasound/activated carbon were applied to remove all dye color and COD from synthetic textile wastewater. The efficiencies of decolorization and COD reduction were accomplished at optimum conditions as 99.9% and 85.22%, respectively.

Keywords: Optimization; Adsorption; Ultrasound; Reactive dye; Decolorization; Statistical modeling

1. Introduction

Synthetic dyes are widely used in the textile and dyestuff industries such as textile dyeing, paper printing, food, cosmetics, pharmaceutical and color photography [1]. Nearly 10,000 different dyes and pigments are used industrially and 0.7 million tons of synthetic dyes are produced each year all over the world [1,2]. Textile wastewater is in first place among industrial wastewater and causes serious environmental problems to destroy aquatic life and consume dissolved oxygen due to its strong color, high COD concentration, a large amount of suspended solids, highly fluctuating pH and high temperature [3,4]. The treatment of textile wastewaters is difficult because of their highly complex structure and it requires special advanced treatment technologies such as adsorption, chemical and photo catalytic methods. Serious environmental problems have led many researchers to treat textile wastewater using traditional treatment methods such as chemical coagulation followed by sedimentation [5], ozonation, adsorption [6], electrochemical oxidation, photo catalytic discoloration [7,8]. These common traditional treatment methods are often ineffective in decolorizing and reducing COD of dyes which are highly the complex and very varied chemical structures [9]. Therefore, many researchers have developed several methods, e.g., UV, ultrasonic decomposition or combined oxidation processes [10] to treat textile wastewater. In recent years, researches have been focused on the treatment of wastewaters using activated carbon [11,12]. It is known that adsorption of dyestuffs on solid adsorbents such as activated carbon is one of the best methods commonly and efficiently used for treatment industrial wastewater. Meanwhile, the implementation of adsorption process has become an increasingly important field, both in order to remove industrial wastes as an alternative to extraction processes, and to solve environmental problems [6]. Adsorption has demonstrated efficiency and economic feasibility as a wastewater treatment process compared to the other purification and separation methods, and has gained importance as a purification and separation process on an industrial application recently [13–16]. Activated carbon is known one of the oldest and most widely applied adsorbents for adsorption of pollutants from wastewater in both industry and laboratory scales [16–19]. In the field of hydrometallurgy, activated carbon has also found important application fields, especially in the recovery of gold and silver from cyanide solutions [20] and such as removal of heavy metals cations from aqueous solution

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by adsorption onto activated carbon from agricultural wastes [21,22]. Nowadays, combined oxidation processes have gained an important application fields, especially in the treatment of dye solutions from textile wastewaters [2,4,23–25].

In recent years, many researchers have actively performed sonochemical treatments on wastewaters treatment. They have reported that various types of chemical contaminant, such as dyes, aromatic compounds, chlorinated hydrocarbons etc., can be decomposed by ultrasound [2,23–25]. Ultrasound produces its mechanical and chemical effects through the formation and collapse of "cavitations" bubbles [26]. A significant amount of research has been published concerning with this "sonochemical effect", and collected in various recent books [27,28]. Ultrasound exhibits also several beneficial mechanical effects in solid–liquid systems by means of the cavitations phenomenon; it causes the formation of many microcracks on the solid surface, thus increases the surface area between the reactants, it cleans solid reactant or catalyst particle surfaces [29]. When water is sonicated $^{\bullet}$H and $^{\bullet}$OH radicals are produced which then undergo a series of reactions ultimately resulting in the production of oxygen gas and hydrogen peroxide [30]. Thus, during the sonochemical treatments of many organic compounds in water, the oxidative decomposition generally proceeds via the reaction with OH radicals which are formed from water pyrolysis in the collapsing hot bubbles. Particularly, in the case of volatile or hydrophobic compounds, the decomposition proceeds not only via OH radicals reaction but also via a direct pyrolysis reaction in the collapsing hot bubbles and at the hot interface region. Although most of the organic compounds can be decomposed by the ultrasonic irradiation, the decomposition rates are still slow for practical uses. Therefore, much effort has been devoted to accelerate the decomposition rates. For example, there are at least three techniques to enhance the reaction rate under ultrasonic irradiation [31–36]: (1) the addition of solid particles or reagents, (2) the combined use of UV irradiation, or (3) the combined use of mechanical agitation. Furthermore, the optimization of the sonication system also includes enhancing the reaction efficiency.

Firstly, it was investigated sonochemical decolorization of a high concentration of azo reactive dye rifacion yellow HE4R from synthetic wastewater to determine optimum decolorization and COD reduction conditions in this research. Afterwards, it was examined combined ultrasound/activated carbon to determine a collective effect of ultrasound and activated carbon on the decolorization and COD reduction. The solid particles or reagent such as activated carbon is especially added in this step to enhance the adsorption rate under ultrasonic irradiation. Activated carbon is used not only in order to decrease process cost and time but also to maximize of decolorization and COD reduction in combined ultrasound/activated carbon process. In this way, the cost of process decreases as the amount of activated carbon decreases. The experiments were planned by using statistical design method. The dye concentration, time, ultrasound power, temperature, activated carbon concentration and initial pH are chosen as process parameters. The regression models obtained were used in a constrained optimization to find optimum process conditions for maximum decolorization and COD reduction efficiency of the reactive dye rifacion yellow HE4R

2. Experimental

2.1. Multivariate experimental design

The factorial experimental design methods are widely used for controlling the effects of parameters in many processes because its usage decreases the number of experiments, time and material resources. In generally, the orthogonal central composite design was widely used for fitting a second-order model. By using this method, modeling is possible and it requires only a minimum number of experiments. It is not necessary in the modeling procedure to know the detailed reaction mechanism since the mathematical model is empirical. These designs consist of a 2^n factorial or fractional (coded to the usual ± 1 notation) augmented by $2n$ axial points ($\pm\beta$, 0, 0. . .,0), (0, $\pm\beta$, 0,. . .,0), ..., (0, 0, ...,$\pm\beta$), and m_0 center points (0, 0,0,. . .,0) [37,38]. Each variable is investigated at two levels. Meanwhile, as the number of factors, n, increases, the number of runs for a complete replicate of the design increases rapidly. In this case, by assuming high-order interactions negligible, main effects and low-order interactions may be estimated by fractional factorial designs. Individual second order effects can not be estimated separately by 2^n factorial designs. Furthermore, the analysis performed on the results is easily realized and experimental errors are minimized. In this paper, the orthogonal central composite design was employed, similar to that described detailed in previous experimental studies [39–42]. The polynomial and optimized conditions were analyzed by using matlab computer software.

2.2. Material and methods

The reactive dye rifacion yellow HE4R was obtained from distributor firm of Itochu with a molecular structure as given in Fig. 1. The characteristics of rifacion yellow HE4R were provided by distributor firm of Itochu and are summarized in Table 1. The activated carbon (Art. 2183) was used as adsor-

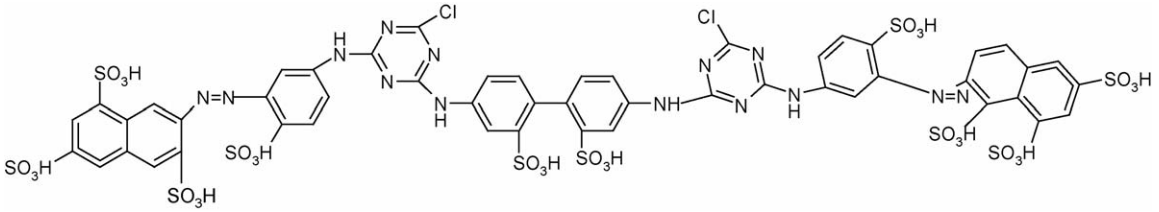

Fig. 1. Molecular structure of reactive dye rifacion yellow HE4R.

Table 1
The characteristics of rifacion yellow HE4R

Parameter	Value
Color index	Reactive Yellow 84
Chromophore	Disazo
Reaktif Anchor systems	ACT[a]
Molar mass (nonhydrolyzed dye)	1922
λ_{max} (nm)	411
Percentage of pure dye (%)	~80
Water solubility at 293 K (g/l)	70
Acute oral toxicity LD_{50} (mg/kg)	–
Fish toxicity LC_0 (mg/l)	–
pH value(10 g/l su da)	–
COD value (mg/g)	160
BOI_5 value (mg/g)	–
DOC value (mg/g)	–

[a] Bisaminochlorotriazine (ACT).

bent all experiments combined ultrasound/activated carbon. The experimental set-up consisted of an ultrasonic power generator (Meinhardt ultraschalltechnic, K 80-5, 140 W, 850 kHz), a jacketed glass reactor equipped with a titan probe (E/805/T/solo ultrasonic transducer), which is connected to the bottom of the reactor and fitted with a reflux condenser. The decolorization and COD reduction of dye solutions were examined under both ultrasound and combined ultrasound/activated carbon conditions. All of the experiments were carried out according to experimental design matrix and the parameters levels shown in Tables 2–3. A typical sonochemical decolorization experiment was carried out in a batch mode as follows: specified amounts of dye solution of known concentration and initial pH were loaded into the glass reactor and maintained the desired decolorization time at the desired temperature. The combined ultrasound/activated carbon experiments were also carried out in a batch mode as follows: specified amounts of dye solution of known concentration and initial pH with activated carbon were loaded into the glass reactor and maintained the desired decolorization time at the desired temperature. Ultrasound power is adjusted by means of the intens of the generator, using the relationship between the intens setting and ultrasound power absorbed by the reaction medium, which is measured by the calorimetric method [43]. A constant temperature circulator was used to maintain the desired temperature in the reactor all the experiments. At the end of the decolorization experiments, the sample was immediately filtered and analyzed.

Table 2
The parameter levels and coded values

Parameters	$+\beta$	+1	0	−1	$-\beta$
Dye concentration[a,b] (ppm) (X_1)	783.6	650	450	250	116,4
Time[a,b] (min) (X_2)	37	30	20	10	3
Ultrasound power[a,b] (W/L) (X_3)	253.2	101.87	25.67	8,53	3,28
Temperature[b] (°C) (X_4)	47	40	30	20	13
Act. carbon conc[b]. (g/L) (X_5)	36,67	30	20	10	3,3
Initial pH[a,b] (X_6)	12	10	7	4	2

[a] Used in only ultrasound on decolorization and COD reduction.
[b] Used in combined ultrasound/activated carbon on decolorization and COD reduction.

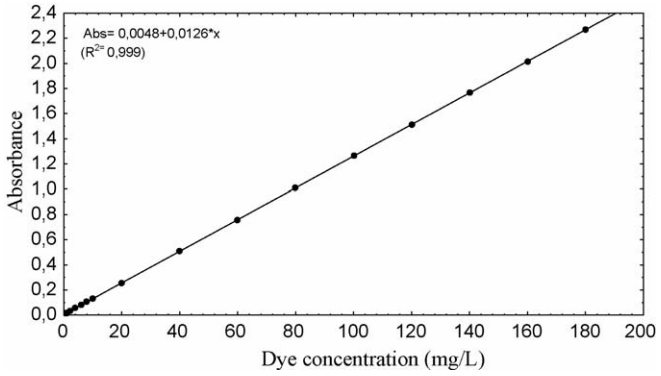

Fig. 2. Calibration curve of reactive dye rifacion yellow HE4R at λ_{max} 411 nm.

2.3. Analytical procedure

The standard stock solutions of 1000 mg/L including rifacion yellow HE4R dye were prepared in distilled water. The standard working solutions were prepared by further dilution of standard stock solutions. The solutions were prepared for calibration curves by further dilution of standard working solutions. The calibration curve established by measuring a series of the solutions is shown in Fig. 2. The initial pH of standard working solutions was adjusted by addition of NaOH or H_2SO_4 to a desired value in the range of 2–12. Samples of dye solutions were measured using a Shimadzu Model UV-160A spectrophotometer at the beginning and at the end of the experiment. COD removal were detected by using Analytic Jena 1100 spectrophotometer and WTW CR 3000 thermoreactor according to standard methods at the beginning and at the end of the experiment [44]. Dye concentrations and COD were calculated from the calibration curves prepared from the dye concentration and the measured absorbance at λ_{max} (411 nm for dye concentration and 600 nm for COD of rifacion yellow HE4R). The percentage of decolorization and COD reduction were calculated as follows:

$$\text{Decolorization\%/COD reduction\%} = \left(1 - \frac{C}{C_0}\right) \times 100 \quad (1)$$

Where C_0 is initial dye concentration/COD (mg/L), C is final dye concentration/COD (mg/L) after US or combined US/activated carbon treatment.

3. Results and discussions

3.1. Response analysis and interpretation

Preliminary experiments were carried out to screen the appropriate parameters and to determine the experimental domain. From these experiments, the effects of dye concentration[a,b] (X_1), time[a,b] (X_2), ultrasound power[a,b] (X_3), temperature[b] (X_4), activated carbon concentration[b] (X_5), and initial pH[a,b] (X_6) are investigated on two responses: the decolorization efficiency and COD reduction. The parameter levels and coded values were given in Table 2.

The 1/2 2^4 orthogonal fractional factorial design and central composite design for ultrasound process and the 1/8 2^6 orthog-

Table 3
Experimental design matrix and response value

	Dye concentration (ppm) (X_1)	Time (min) (X_2)	Ultrasound power/volume (W/L) (X_3)	Temperature (°C) (X_4)	Activated carbon concentration (g/L) (X_5)	InitialpH (X_6)	Decolorization efficiency%
1	0	0	0	0	0	0	45.52
2	−1	1	−1	−1	1	−1	82.91
3	−1	1	1	−1	−1	1	61.89
4	0	0	0	0	0	0	45.83
5	−1	−1	−1	1	1	1	73.91
6	1	−1	−1	−1	−1	1	81.13
7	1	1	1	1	1	1	78.14
8	1	1	−1	1	−1	−1	88.97
9	−1	−1	1	1	−1	−1	86.69
10	1	−1	1	−1	1	−1	78.56
11	0	0	0	0	0	0	50.23
12	+β	0	0	0	0	0	52.56
13	−β	0	0	0	0	0	41.77
14	0	+β	0	0	0	0	58.65
15	0	−β	0	0	0	0	46.88
16	0	0	+β	0	0	0	60.89
17	0	0	−β	0	0	0	50.16
18	0	0	0	+β	0	0	46.03
19	0	0	0	−β	0	0	43.13
20	0	0	0	0	+β	0	67.33
21	0	0	0	0	−β	0	17.71
22	0	0	0	0	0	+β	72.83
23	0	0	0	0	0	−β	99.24

onal fractional factorial design and central composite design for combined ultrasound/activated carbon process were applied to estimate both main effects and second order effects as well as interaction effects. Furthermore, three central replicates were also employed to calculate pure experimental error. As usual, the selected experiments were performed randomly in order to minimize the effect of systematic error. The experimental design matrix and the corresponding experimental parameters and response value were shown in Table 3. Matlab computer software was used to model and optimize the experimental results.

At the end of sonochemical decolorization, the regression model for decolorization efficiency (Y_{de}) of reactive azo dye rifacion yellow HE4R founded with effective parameters obtained by variance analysis tested at 90% confidence level was given as follows. The correlation coefficient (r^2) of model obtained in this case is 0.99.

$$Y_{de} = 0.98 - 1.6680X_1 + 4.1044X_2 + 5.0230X_3 - 4.1038X_6 + 3.8943X_1^2 + 1.5611X_2^2 + 2.1849X_3^2 + 4.4257X_6^2 - 3.6250X_1X_3 + 3.6750X_1X_6 + 3.6750X_2X_3 - 3.6250X_2X_6 \quad (2)$$

Fig. 3 illustrates the graphical representation of 'size effect' of each of parameters upon the decolorization by alone ultrasound. From Fig. 3 it can be seen that dye concentration (X_1), initial pH (X_6) have a negative effect, while time (X_2) and ultrasound power (X_3) have a positive effect on the response: the decolorization efficiency of the reactive dye rifacion yellow HE4R. The second order terms and interaction terms affect to the process at various ratios. At the end of the sonochemical decolorization, our experimental results confirm the suitability of ultrasound for removal of dye color, but ultrasound alone was insufficient method to remove all dye color and COD from textile wastewater. Therefore, activated carbon was added to accelerate the decomposition rates for adsorption of dye color which is decomposed sonochemically [31–36]. At the end of combined

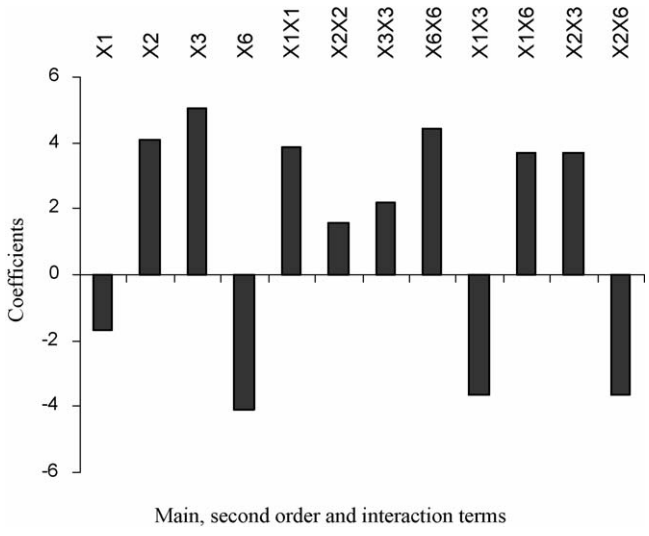

Fig. 3. Significant main, second order and interaction terms for sonochemical decolorization of reactive azo dye rifacion yellow HE4R.

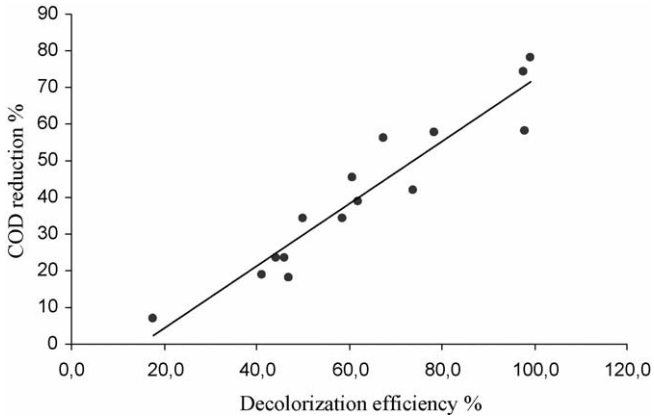

Fig. 4. A linear relation between the COD reduction efficiency and decolorization efficiency.

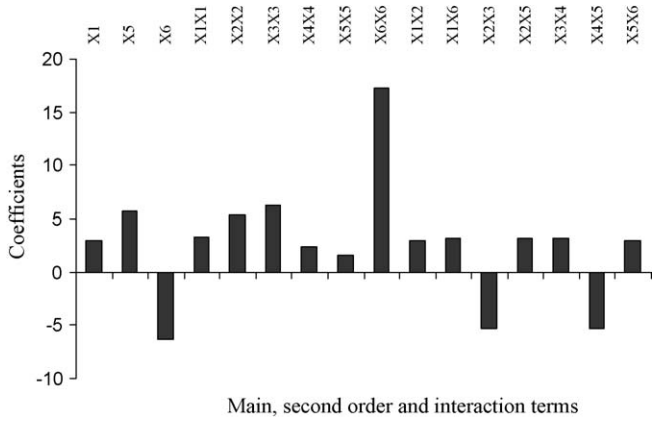

Fig. 5. Significant main, second order and interaction terms for decolorization and COD reduction of reactive azo dye rifacion yellow HE4R by using combined ultrasound/activated carbon.

ultrasound/activated carbon experiments, the model established with effective parameters obtained by variance analysis tested at 90% confidence level was given as follows. The correlation coefficient (r^2) of model obtained in this case is 0.9159.

$$Y_{de} = 40.96 + 2.9045X_1 + 5.7213X_5 - 6.3483X_6 + 3.2761X_1^2 + 5.2888X_2^2 + 6.2808X_3^2 + 2.3470X_4^2 + 1.6066X_5^2 + 17.2464X_6^2 + 2.9025X_1X_2 + 3.1925X_1X_6 - 5.2575X_2X_3 + 3.1925X_2X_5 + 3.1925X_3X_4 - 5.2575X_4X_5 + 2.9025X_5X_6 \quad (3)$$

According to combined ultrasound/activated carbon experimental results, the COD reduction efficiency is a linear function of the decolorization efficiency, as expected. To test this suggestion, the COD reduction efficiency is plotted versus decolorization efficiency as in shown in Fig. 4. A linear regression between the COD reduction efficiency (Y_{COD}) and decolorization efficiency (Y_{de}) is as the following relation:

$$Y_{COD} = 0.9158\,Y_{de} - 16.024 \quad (r^2 = 0.9307) \quad (4)$$

Where Y_{de} represents decolorization efficiency, Y_{COD} represents COD reduction efficiency.

Fig. 5 shows the graphical representation of 'size effect' of each of parameters upon the decolorization and COD reduction by applying combined ultrasound/activated carbon. From this figure it can be seen that dye concentration (X_1), activated carbon concentration (X_5) have a positive effect, while initial pH (X_6) has a negative effect on two responses: the decolorization efficiency and COD reduction of the reactive dye rifacion yellow HE4R. The second order terms and interaction terms affect to the process at various ratios.

3.2. Optimization

The main objective of this research is to determine the experimental conditions required to remove dye color and COD. Then, using above mentioned methodology for experimental design, the ranges of the parameters required to obtain optimum conditions were determined. In this optimization study, decolorization efficiency and COD reduction of the reactive dye rifacion yellow HE4R solutions were chosen as the objective function. Furthermore, optimum conditions are often calculated in the presence of some constraints which ensure them to be more realistic. If the model used in the optimization study is an empirical one, high and low levels of the process parameters in the experimental design are considered, inevitably, as explicit constraints, in order to avoid extrapolation.

Thus, the optimization problem is defined both responses as;

- Maximize

$$Y_{de}/Y_{COD} \quad (5)$$

- Constraints on the parameters X

$$-\beta_i < X_i < +\beta_i \quad i = 1 \ldots 6 \quad (6)$$

$-\beta$ and $+\beta$ values are given in Table 2. The optimization problem (5) is solved using constrained optimization program supplied in the Matlab optimization toolbox. These results show that; ultrasound power is effectively used at its lower

Table 4
Optimum conditions for decolorization and COD reduction of reactive azo dye rifacion yellow HE4R

	Dye conc. (ppm)	Time (min)	Ultrasound power/ volume (W/L)	Temp. (°C)	Act. carbon Conc. (g/L)	Initial pH	Decolor. Eff.%	COD reduc.%
Only ultrasound	155	35	253	20	–	2.6	80.62	Insufficient
Combined ultrasound/ Activated carbon	783.6	20	25.67	30	36.7	2	99.9	85.22

Table 5
Freundlich constants for reactive azo dye rifacion yellow HE4R adsorption on activated carbon

K_f	0.0563
n	1
Equilibrium range (ppm)	67–372
r	0.913

bound, medium decolorization time, temperature are sufficient for decolorization efficiency and COD reduction of the reactive dye rifacion yellow HE4R solutions, whereas dye concentration, activated carbon and initial pH have more strong impacts on the optimum decolorization and COD reduction. The optimum process conditions are given in Table 4 by taking into account the models given in Eqs. (2)–(4) established with effective parameters obtained by variance analysis conducted at 90% confidence level. Maximum decolorization efficency and COD reduction under combined ultrasound/activated carbon are 99.9% and 85.22%, respectively, but they have been found 80.62 under ultrasound alone and only ultrasound was insufficient to remove COD. The dye adsorption capacity on per gram of the activated carbon was obtained as 57 mg/g and the experimental adsorption data were fitted to Freundlich adsorption isotherm. Table 5 presents the constants of Freundlich adsorption isotherm for the reactive dye rifacion yellow HE4R on activated carbon by ultrasound-assisted adsorption. According to the optimum process conditions given in Table 4, dye concentration decolorized under combined ultrasound/activated carbon process is approximately five times greater than that of the dye concentration decolorized under ultrasound alone. In this case, decolorization efficiency increased with the decrease of time and ultrasound power under combined ultrasound/activated carbon process. In conclusion, it is thought that ultrasound irradiation enhanced decolorization of dye over activated carbon via physical and chemical effects of sonication.

4. Summary and conclusions

A high concentration of the reactive dye rifacion yellow HE4R was examined under ultrasound and combined ultrasound/activated carbon. 80.62% decolorization efficiency was accomplished by ultrasound. But alone ultrasound was insufficient for removal dye color and COD reduction. Then, combined ultrasound/activated carbon was applied to remove all dye color. The decolorization efficency and COD reduction are much higher in the presence of combined ultrasound/activated carbon than using ultrasound alone. Ultrasound irradiation enhanced decolorization of dye over activated carbon via physical and chemical effects of sonication. The experimental results show that combined ultrasound/activated carbon are an efficient process to remove all dye from textile wastewater as 99.9%. If ultrasound power is effectively used at its lower bound, the dye concentration, activated carbon concentration and initial pH are important process parameters that affect the decolorization and COD reduction. The proposed combined ultrasound/activated carbon process may be applicable in the treatment of textile wastewater. Considering the economical aspects, the use of combined ultrasound/activated carbon process may seem expensive. Therefore, this combined ultrasound/activated carbon process cost can be cheapen by producing activated carbon from cheaper and readily available agricultural by-products to use as adsorbent in combined ultrasound/activated carbon process for removal of dye color and COD reduction. However, detailed optimization researches along with cost analysis are needed to decide on the profitability of using ultrasound and activated carbon. It is expected that the optimization results presented in this paper may provide background information for a detailed decolorization and COD reduction process improvement research.

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