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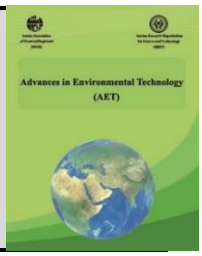

Desorption of reactive red 198 from activated Carbon prepared from walnut shells: Effects of temperature, Sodium carbonate concentration and organic solvent dose

Zohreh Alimohammadi, Habibollah Younesi*, Nader Bahramifar

Department of Environmental Science, Faculty of Natural Resources, Tarbiat Modares University, Noor, Iran

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ABSTRACT

This study investigated the effect of temperature, different concentrations of sodium carbonate,and the dose of organic solvent on the desorption of Reactive Red 198 dye from dye-saturated activated carbon using batch and continuous systems. The results of the batch desorption test showed 60% acetone in water as the optimum amount. However, when the concentration of sodium carbonate was raised, the dye desorption percentage increased from 26% to 42% due to economic considerations; 15 mg/L of sodium carbonate was selected to continue the process of desorption. Increasing the desorption temperature can improve the dye desorption efficiency. According to the column test results, dye desorption concentration decreased gradually with the passing of time. The column test results showed that desorption efficiency and the percentage of dye adsorbed decreased; however, it seemed to stabilize after three repeated adsorption/desorption cycles. The repeated adsorption–desorption column tests (3 cycles) showed that the activated carbon which was prepared from walnut shell was a suitable and economical adsorbent for dye removal.

1. Introduction

Dye wastewater discharged from textile and dyestuff industries are one of the most significant sources of pollutants in the environment [1]. Reactive dyes are extensively used in textile industries because of their exclusive properties which include bright color and low energy consumption [2]. It is estimated that around 40% of consumed reactive dyes are discharged into the wastewater of dyeing operations [3]. Reactive dyes are soluble in water, so removing them by flocculation and biodegradation is very difficult. The presence of dye in water can cause many problems including high biochemical oxygen demand (BOD), chemical oxygen demand (COD) and an increase in suspended solids [4]; thus, effective treatment methods such as flocculation, membrane separation processes, oxidation, electrolysis and adsorption are needed to remove them from wastewaters [5]. Among the mentioned methods, adsorption by adsorbent is one of the most effective methods for removing dye molecules. A successful sorbent material should have a high affinity and capacity for adsorbate molecules as well as regeneration potential. Also, it should be applicable for the majority of reactive dyes and economically affordable [6]. Activated carbon (AC) is an appropriate adsorbent for dye adsorption because of its large surface area, appropriate porosity and hydrophobic properties [7]. ACs can be prepared from a wide range of low-cost carbonaceous material such as agricultural waste. Two processes are commonly used for the preparation of ACs: physical activation that includes material carbonization and chemical activation in which the raw material is impregnated with activating agents such as $ZnCl_2$, H_3PO_4, KOH, K_2CO_3 [8]. In this research, the AC was prepared from walnut shells by chemical activation with KOH (AC –K1). The results of the adsorption of RR198 by activated carbon developed from walnut shells were presented in our

*Corresponding author. Tel: +98(11)44553101-3
E-mail address: hunesi@modares.ac.ir, hunesi@yahoo.com

published report [9]. The results showed that AC –K1 with a surface area of 1439 m^2/g has an increased ability to remove RR198 from wastewater. A desorption study can help us to explain the nature of the adsorption and recycling of the dye saturated adsorbent [10]. However, desorption of the AC saturated with dye not only can regenerate the adsorbent but can also return the dye back into the dyeing process. Then, desorption of the dye from AC saturated with dye becomes economically affordable [11]. The objective of this study was to investigate the effect of organic solvent, sodium carbonate, and temperature on desorption of reactive red 198 dye (RR198) from AC made from walnut shells in batch and column systems.

2. Materials and methods

2.1. Materials

Walnut shells collected from a fruit grower in the north of Iran were used as raw material for the preparation of the AC. This agricultural waste was washed with distilled water to remove dust and other inorganic impurities, then it was dried in an oven at 110°C to reduce its moisture content; finally, it was crushed and sieved to a particle size of 0.4–0.8 mm. The reactive red 198 ($C_{27}H_{18}C_lN_7Na_4O_{15}S_5$, molecular weight of 967.5 g/mol) was purchased from the local market. The RR198 characteristic and structure is illustrated in Table 1 and Figure 1. The potassium hydroxide (KOH) was purchased from Scharlo, Spain. The sodium hydroxide (NaOH), hydrochloric acid of 37% (HCl), sodium carbonate (Na_2CO_3) and acetone of 99.5% were purchased from Merck, Germany.

Table.1. Characteristics of Reactive Red 198

Characteristic	Reactive Red 198 (RR-198)
Molecular formula	$C_{27}H_{18}C_lN_7Na_4O_{15}S_5$
Color index name	Reactive Red- 198
λ_{max}	520 nm
Class	Monoazo (-N=N-bond)

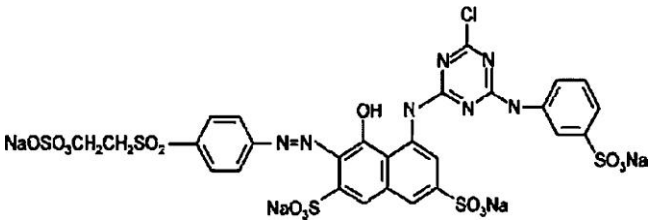

Fig. 1. Structure of reactive red dye

2.2. Preparation of Activated Carbon

Activated carbon was prepared by mixing a certain weight of walnut shell with impregnation ratios of KOH: walnut shell 1 g/g. The impregnated walnut shell was dried at 110°C for 24 hours and pyrolyzed under an argon atmosphere in a furnace at a temperature of 900˚C at an increment rate of 10˚C/min for a 1 hour retention time. Then, the samples were removed from the reactor and washed with hot and cold distilled water until the water pH reached about 6-7 in order to remove impurities of the synthesized activated carbon. Finally, the washed samples were dried in an oven at 110˚C, weighed and kept in a capped bottle for subsequent use. The sample was named AC –K_1.

2.3. Batch desorption tests

Before the desorption tests, 0.1 g of AC –K1 was added to 250 mL flasks containing 100 mL of RR198 wastewater with a 40 mg/L concentration at a pH=3 and a temperature of 50˚C. The flasks were shaken at 120 rpm for 60 min until adsorption reached equilibrium. After filtration, a spectrophotometer device was used (at 520 nm wavelength) to determine the residual dye concentrations in the solutions. The separated activated carbon was added to 100 mL flasks filled with 20 mL of the regenerate with desired concentrations; then the flasks were shaken at 120 rpm for 40 min. After filtration, the dye concentrations in the solutions were measured. Desorption experiments were performed for different temperatures (20, 30, 40, 50 and 60 °C) and certain concentrations of sodium carbonate (5 to 20 mg/L) and organic solvent (30%-80% acetone in water). The desorption efficiency (DE) was determined with the following equation:

$$\mathrm{DE}\% = \frac{A_0 - A_d}{A_0} \times 100 \quad (1)$$

where A_0 and A_d are the amount of dye adsorption and residual dye concentrations in the solutions after desorption, respectively.

2.4. Column tests

Continuous adsorption/desorption experiments were carried out in a double glazed glass column with a 2 cm inner diameter and 20 cm height. The RR198 solution of a certain concentration (40 mg/L) was pumped into a column filled with AC –K1 with a height of 2 cm at a constant flow rate (1 mL/min) using a peristaltic pump (Pump drive PD 5101 Heidolph peristaltic, Schwabach, Germany) until the column was saturated with the dye solution. Also, the top and bottom of the adsorbent was filled with glass wool. Adsorption experiments were carried out at a temperature of 50°C and a pH = 3. Then the saturated column was regenerated with the optimal regenerant solution with 60% acetone in water and 15mg/L sodium carbonate. The column temperature during the tests was 50 °C. After the regeneration of each column, hot water was used to wash the carbon in the column in order to remove the regenerant solution before the next adsorption cycle. The regeneration cycles were repeated three times.

3. Results and discussion

3.1. Dye desorption in batch experiments

3.1.1. Effect of organic solvent dose

The complex structure of RR198 dye makes its removal difficult by organic solvent. Due to the effectiveness of acetone on desorption of activated carbon, acetone was selected for desorption of the dye-saturated activated carbon. Since the dilution of pure solvents with water can increase the desorption efficiency, the effect of organic solvent concentration was investigated in the range of 30%-80% (volume percentage) acetone in water. As shown in Figure 2, the most effective solvent dose for desorption of the RR198 from the activated carbon was 60% acetone in water. Desorption efficiency decreased when a high percentage of acetone in water was applied for the process. This trend may be due to reducing the ability of activated carbon in the low percentage of water condition. Similar observations have been reported for the effect of organic solvents on desorption of red dye on activated carbon in which the maximum desorption efficiency percentage was observed at 60% acetone in water [12].

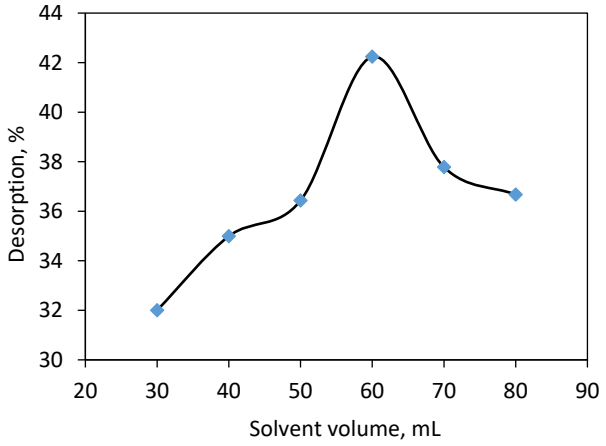

Fig. 2. Effect of solvent dose on the desorption efficiencies of the red dye at 25 °C

3.1.2. Effect of sodium carbonate concentration

The selection of an appropriate base for desorption of the dye from activated carbon was made by considering its dependency with the dye structure. According to this study, we found that pH has a great influence on the dye adsorption onto activated carbon and the High removal percentage is observed at acidic pH condition [9]. The reduced pH level in the acid condition caused an increase of H^+ ion concentration in the solution and therefore, the surface of the adsorbent achieved a positive charge and tended to attract the negatively charged groups of the RR198 structure. Hence, bases appeared to be appropriate solutions for desorption of the RR198 from the saturated carbon activate. The addition of sodium carbonate to aqueous acetone solutions greatly improved the dye desorption performance. The effect of different sodium carbonate concentrations on desorption in 60% acetone is shown in Figure 3. It can be observed from Figure 3 that the dyes desorption percentage increased from 26% to 42% when the sodium carbonate concentration was raised from 5 to 20 mg/L. This phenomenon can be attributed to the presence of _SO_3Na functional groups in RR198 in which a high concentration of sodium carbonate caused an increase negative charge on the surface of the adsorbent. This was beneficial for desorption of anionic dye molecules. Similar trends have been reported for the effect of NaOH on desorption of reactive red dye on activated carbon [13]. Also, similar observations were obtained for desorption of anionic reactive dyes (Cibacron blue 3GA and Cibacron red 3BA) by mixtures of NaOH in a methanol solution [14].

3.1.3. Effect of temperature

In order to increase the desorption efficiency, batch experiments were performed at 20, 30, 40, 50 and 60°C using 60% acetone in a water solvent and 15 mg/L of sodium carbonate. Since the adsorption of RR198 onto AC is an endothermic process, it is expected that dye desorption falls when temperature increases. But according to Figure 4, the dye desorption percentage increased with an increase in temperature and thus, the maximum dye desorption percentage was observed at 60°C. This trend can be related to the increase of acetone solubility in water with the rising of temperature that led to an increase in desorption efficiency. Given that there is not much difference between the dye percentage at 60 and 50°C because of economic consideration, 50°C was selected as the optimal temperature.

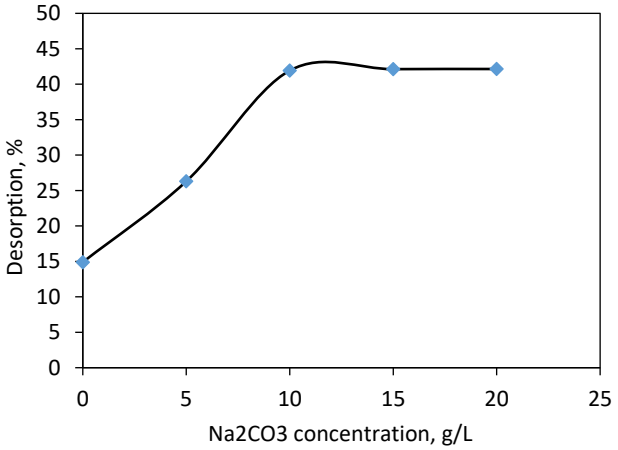

Fig. 3. Effect of sodium carbonate concentration on the desorption efficiencies of the red dye (25 °C, 60% aceton)

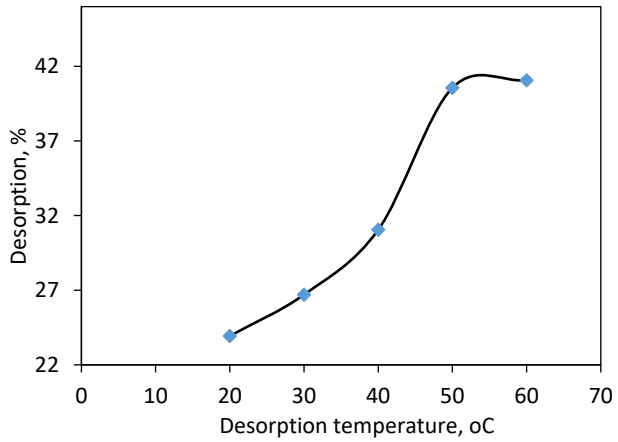

Fig. 4. Effect of temperature on the desorption efficiencies of the red dye (15 mg/L sodium carbonate, 60% aceton)

3.2. Column experiments

Based on the batch test results, the optimum conditions for desorption of dye-saturated activated carbon were found to be 60% acetone in water, 15 mg/L of sodium carbonate and 50°C. As seen in Figure 5, the maximum concentration of desorbed dye (more than 32 mg/L) occurred in the first five minutes; then it gradually decreased as time passed and the total desorption time was 75 minutes. Figure 6 illustrates the regeneration efficiency of red dye for the repeated adsorption/desorption cycles. Figure 6 indicates that the regeneration efficiency decreased from 44.99% to 28.52% and the amount of dye adsorbed decreased from 71.3% to 66.5% after the three repeated adsorption–desorption cycles but after three cycles, adsorbent Has low efficiency in dye adsorption. Additional repeating of the adsorption–desorption column tests with the optimal regenerant showed the ability of AC –K1 to efficiently adsorb and desorb the dye molecules and AC –K1 can be used repeatedly for the removal of dye from waste water. Similar trends have been reported for the desorption of Pb(II) ions on activated tea waste [15].

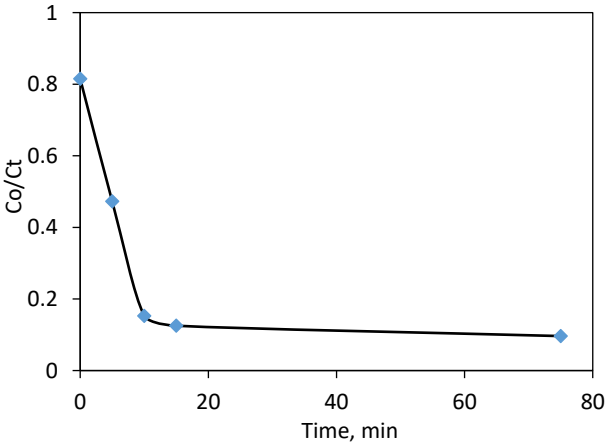

Fig. 5. Desorption curve of column operation (60% acetone, 15 mg/l sodium carbonate, 50 °C)

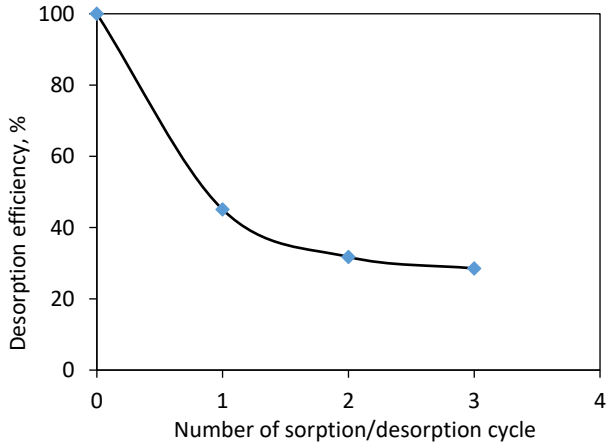

Fig. 6. Adsorption–desorption cycles (60% acetone, 15 mg/l sodium carbonate, 50 °C)

4. Conclusions

The activated carbon was prepared from walnut shell, as a low-cost raw material, using the activating agent KOH. The desorption of RR198 dye from the AC was performed in batch and continuous systems. The batch desorption test results showed that 60% acetone in water and 15 mg/L of sodium carbonate were the optimal regenerants for the red dye. An increase in desorption temperature increased desorption efficiency. The results of the column desorption test demonstrated that the concentration of dye desorbed from the activated carbon decreased as time passed. The percentage of desorption efficiency was decreased after three repeated adsorption/desorption cycles using the optimal regenerant.

Nomenclature

Acronyms	
Obs	Observed values of growth
Mean obs	Mean of observed values
Pred	Predicted values of growth
n	Number of samples
Notations	
A	Asymptotic ln X_t/X_0 as t decreases indefinitely −
A(t)	Precise integral of the adjustment factor h
B	Relative growth rate at time M h^{-1}
C	Asymptotic ln X_t/X_0 as t increases indefinitely −
K	Time at which half maximum growth is achieved h
M	Time at which absolute growth rate is at its maximum h
T	Residence time h

X_0	Initial cell concentration mg L^{-1}
X_{max}	Maximum cell concentration mg L^{-1}
X_t	Cell concentration at time t mg L^{-1}
Y	$\ln(X_t/X_0)$ –
Greek symbols	
λ	Lag phase duration h
μ_{max}	Maximum-specific growth rate h^{-1}
ν	Shape or curvature parameter –

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