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Comparison Between the Performance of Activated Carbon and Graphene in Removal of Reactive Red 198

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Abstract

The current study aimed at comparing the performances of activated carbon and graphene in the removal of reactive red 198. The experiments were conducted in a batch reactor and the effects of some operational parameters including initial dye concentration, pH, contact time, and different doses of activated carbon and graphene on the removal efficiency of dye were investigated. The results showed that the adsorption efficiency was affected by initial dye concentration. In general, with increasing contact time up to 180 minutes, the removal efficiency increased significantly. The removal efficiency of reactive red 198 increased with increasing contact time, and after 60 minutes of contact time, adsorption phase reached the equilibrium. When activated carbon was used, the maximum removal efficiency happened at pH 3. At this pH value, reactive red 198 was removed completely (100%) after 120 minutes, whereas the minimum efficiency was observed at pH 10. A similar trend was also observed for graphene as an adsorbent. Moreover, the removal efficiency of the dye by both adsorbents increased with the increase of the adsorbent dosage. The experimental data showed that the adsorption of reactive red198 on both active carbon and graphene fitted well into the second-order kinetic model. Active carbon and graphene fitted well Langmuir 1 model. According to the results, graphene acts as suitable adsorbent and can be applied in treating several industrial effluents and contaminated water in greater scales. The main upside of grapheme, in comparison with activated carbon, is that it reaches the equilibrium in a shorter time. Further, grapheme adsorbed the dye nearly completely (98% to 100%).

Keywords: Reactive Red 198, Activated Carbon, Graphene, Adsorption

1. Introduction

Several industries, such as pharmaceutical, leather-making, paper-making, and especially textile, produce huge values of wastewater containing various dyes, which are entered into the environment and cause many problems (1-3); treatment of these kinds of wastewater is of great importance. Dyes are a group of toxic organic compounds that have complex aromatic structures, and are chemically and photochemically stable (4-6).

Textile dyes are classified into 3 categories (1, 7) anionic: acid, direct and reactive dyes are applied to fibers such as silk, wool, and nylon; (2, 8) cationic: basic dyes are mainly applied to acrylic fibers and (3) non-ionic: disperse dyes, which improve the fastness of the dye against water, light, and perspiration (9). Reactive dyes are of the most widely used materials as more than 10,000 dyes are applied in textile processing industries (10). Discharge of wastewater containing textile dyes into the environment and surface waters can disturb the ecology of acceptor waters, because they have adverse effects on aqueous ecosystem. Moreover, previous studies reported that the textile dyes were toxic to humans. In recent years, various technologies are examined to remove these dyes from industrial wastewaters such as advanced oxidation, electrochemical coagulation, oxidation coagulation, biological degradation, and membrane processes, which each of them has several disadvantages and limitations (4, 11).

Adsorption is one of the most common technologies used to treat wastewaters containing textile dyes. Previous studies suggested that the adsorption process can be used as an alternative process to remove reactive dyes. In this regard, activated carbon, as an adsorbent, is widely used to remove pollutants from water and wastewater (12). Graphene is an allotrope of carbon materials, in form of 2-dimensional, with nanopores. Due to its special properties such as high surface area, high porosity, thermal stability, mechanical strength, and high electrical conductivity it is considered highly.

The current study investigated the performance of activated carbon and graphene in the removal of reactive red 198. Moreover, the effects of some operational parameters including initial dye concentration, pH, contact time, and different doses of activated carbon and graphene on the removal of reactive red 198 were investigated.

2. Materials and Methods

2.1. Preparation of the Dye

Reactive red 198 used in the current study was purchased from Alvan Sabet Co., Hamadan, Iran. The dye was dried in an oven at 110°C for 1 hour.

2.2. Batch Experiments

The current experimental research was conducted at chemical laboratory of the environmental health engineering department, Hamadan University of Medical Sciences. All experiments were conducted in a pilot scale reactor.

The effect of some operating parameters including initial dye concentration (25, 50, 75, 100 mg/L), pH (3, 7, 10), adsorbent dose, and contact time (0 to 450 minutes) on the dye adsorption by means of graphene and activated carbon were investigated separately for each adsorbent and all the parameters were optimized as a method (13).

In the 1st steps of the experiments, to study the equilibrium time, 250 mL of reactive red 198 solutions (50 and 100 mg/L) were prepared, and 0.02 g of graphene and 0.2 g of activated carbon were added to each solution in separate phases; it should be noted that grapheme has a higher adsorption capacity than activated carbon, which, in turn, a lower amount of this adsorbent was required. These compounds were mixed and the concentration of the remaining dye was measured after 5, 10, 20, 30, 45, 60, and 480 minutes. This process was continued until adsorption rate became zero. Next, the stoke solution of reactive red 198 was prepared by dissolving 1000 g of the solid dye in distilled water. After that, to study the effects of initial concentrations of the dye, various contents of reactive red 198 (25, 50, 75, and 100 mg/L) were prepared by dissolving the stock solution in certain amounts of distilled water. Finally, the effect of solution pH (3 - 10) was studied on the efficiency of both activated carbon and graphene in the dye adsorption.

2.3. Analysis

To separate grapheme and carbon from the samples after the reactions, a centrifuge device was used (1400 rpm for 15 minutes).

The concentration of reactive red 198 was measured using a UV/vis detector at the wavelength of 518 nm. Dye removal efficiency was calculated according to the following equation:

$$(\%) = \frac{C_0 - C_t}{C_0} \times 100 \qquad (1)$$

Where, C_0 and C_t are, respectively, the initial and final concentrations of the dye.

3. Results and Discussion

3.1. Effect of Dye Concentration

At this stage, the effect of different concentrations of reactive red 198 in the range of 25 to 50 mg/L on the adsorption process by both adsorbents (activated carbon and graphene) was studied. The results shown in Figure 1 illustrate that when activated carbon was used as an adsorbent, the adsorption efficiency increased with an increase in initial dye concentration. Therefore, it can be pointed out that the adsorption efficiency was affected by the initial concentration of dyes (14). In general, with increasing contact time up to 180 minutes, the removal efficiency increased significantly. As shown in Figure 1, the maximum efficiency was observed at 75 mg/L of the dye after 450 minutes, which was 96%. In contrast, during this contact time 80% of the dye was removed at the minimum at initial concentration of 25 mg/L. This phenomenon can be attributed to the low number of dye molecules at low concentrations to adsorb the activated carbon (15). The adsorption efficiency for graphene is presented in Figure 2. As shown, the efficiency of reactive red 198 increased with increasing the contact time. After 60 minutes of contact time, adsorption phase reached the equilibrium. Moreover, in the case of using graphene as an adsorbent, the adsorption efficiency was not obviously related to initial dye concentration. The graphene efficiency in adsorption of reactive red 198 in all studied concentrations of the dye was in the range: 98% to 100%; this can be considered as a special feature of this adsorbent in removing pollutants (16). Similar results were also obtained in the author' previous study, in which the removal efficiency of acid orange 7 by graphene was investigated (17).

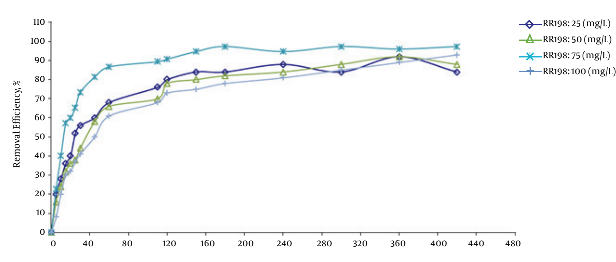

Figure 1. Effect of Different Concentrations of Reactive Red on Adsorption Process Using Actived Carbon (pH: 7, Adsotbent Concentration: 0.24 mg/L)

3.2. Effect of pH

The effect of solution pH in the range of 3 to 10 on dye removal was investigated. The results are indicated in Figures 3 and 4. As can be observed, in the case of activated carbon, the maximum removal efficiency (100%) happened at pH 3 after 120 minutes, whereas the minimum efficiency was observed at pH 10. A similar trend was also observed for graphene; as shown in Figure 4, the maximum efficiency was obtained at pH 3. The minimum efficiency was observed at pH 10 equal to 84%. Moreover, pH_{zpc} is one of

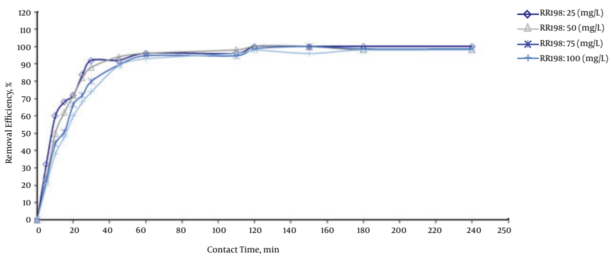

Figure 2. Effect of Different Concentrations of Reactive Red on Adsorption Process Using Geraphene (pH: 7, Adsotbent Concentration: 0.24 mg/L)

the surface characteristics of absorbents, which at higher values than pH_{zpc}, the adsorbent has a negative charge and it is positive at lower values (18). In order to determine this parameter, 30 mL of 0.01 M NaCl solution was added to a 50-mL Erlen-meyer flask and the pH values of the solutions were adjusted between 2 and 12 using H_2SO_4 and NaOH. Next, the optimum amount of each adsorbent was also added to the Erlen-meyer flask and the solutions were shaken for 48 hours at 120 rpm. Then, the final pH values were read by a pH-meter. The point of pH_{ZP} of the adsorbent was calculated by drawing the initial pH values verses final pH values (Figure 5).

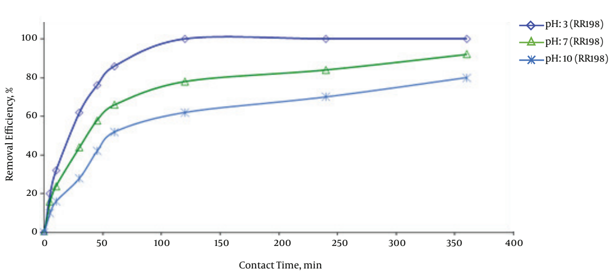

Figure 3. Effect of Different pH Values on Adsorption Process Using Geraphene (Dye Initial Concentration: 50 mg/L, Adsotbent Concentration: 0.24 mg/L)

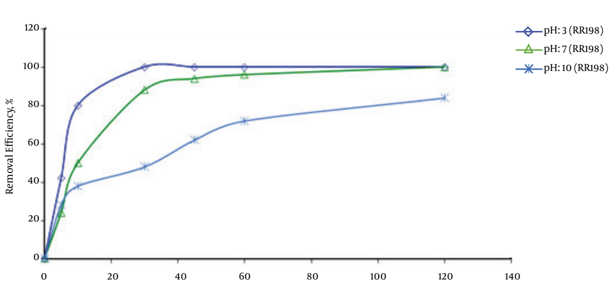

Figure 4. Effect of Different pH Values on Adsorption Process Using Geraphene (Dye Initial Concentration: 50 mg/L, Adsotbent Concentration: 0.8 mg/L)

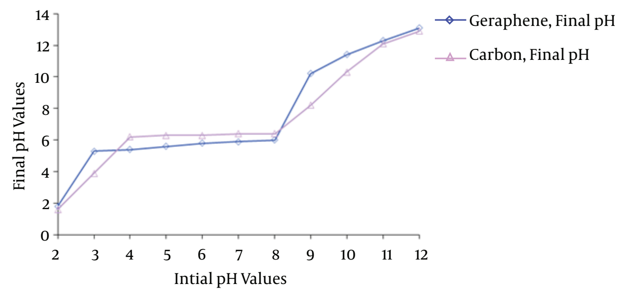

Figure 5. Efficiency of Graphene and Active Carbon at Different pH Values

The values of pH_{zpc} for graphene and activated carbon were 6 and 6.3, respectively. Due to the fact that the dye used in the current study was anionic, its high efficiency at pH 3 can be attributed to the presence of ions with opposite electric charge at the adsorbent surface. It can be said that the removal efficiency for both activated carbon and graphene decreased with pH increase. This may be related to the increase of positive charges on the adsorbents at lower pH values.

Since, at low pH values, due to protonation of amine and hydroxyl groups, positive charges increased in the adsorbent, and a suitable electrostatic adsorption was created between the adsorbent and anionic dye (19). Another reason for it is that the charge of surface and amount of ionization of changes and dyestuff change with the level of pH increase.

Similar results were obtained by Chompuchan et al. (20) who investigated decolorization of reactive black 5 and reactive red 198 using nanoscale zerovalent iron. Mehrizad A et al., surveyed the degradation of 4-chloro-2-nitrophenol from aqueous solution by graphene; they reported an increase in removal efficiency by increasing solution pH from 3 to 10 (21).

3.3. Effect of Contact Time

As can be observed (by by means of activated carbon, the dye was absorbed quickly in the 1st steps; then, its rates decreased and reached the equilibrium at a lower rate. The findings showed that the highest amount (92%) of the efficiency was attained at initial dye concentration of 50 mg/L, and contact time of 360 minutes, whereas the adsorbent of graphene could remove 100% of the dye at initial dye concentration of 50 mg/L, and contact time of 100 minutes. Moreover, in the case of graphene, the adsorption process reached the equilibrium quickly, but the time for activated carbon to reach adsorption equilibrium was approximately 300 to 420 minutes. It can be concluded that graphene can be entirely effective in the removal of this dye in lower contact time (22). This high removal efficiency can be attributed to physicochemical properties of this adsorbent, because its high surface area, as well as porosity, increases the number of active adsorption sites available for dyestuff (23). Further increase in contact time did not show significant change in equilibrium concentration; that is, the adsorption phase reached equilibrium. This phenomenon is linked to the high number of unoccupied active sites on adsorbent's surface at the early stages of the process. Over the time, the remaining active sites are occupied by the adsorbent with difficulty, which is because of the repulsive force among the molecules of the soluble material and the dye in solid phase (24).

3.4. Effect of Graphene and Active Carbon Concentration

The content of adsorbent is one of the important factors in dye adsorption; this is owing to the determining role of adsorbent capacity in adsorbing contaminants on its surface.

The concentration of adsorbents determines the capacity of active carbon when it is applied as an adsorbent. In the current study, special amounts of the dye were absorbed (25). In general, the removal efficiency went up when there was an increase in the amount of active carbon from 0.2 to 4 g/L. The number of available sites, which are active, increases at high concentrations of active carbon. In addition, to study the effect of graphene dose on dye removal, 0.02 to 0.4 g/L of this adsorbent was examined under optimized conditions. The findings showed that the efficiency went up from 64% to 84%; this can be owing to high surface area of the used adsorbent. Furthermore, at higher contents of the adsorbent, the adsorption capacity declined, which is due to the overlap of adsorptive sites on the adsorbent's surface. Of course, it can be also attributed to the decreasing impact of the slope between dye molecule and adsorbent concentrations (26). The results of the current study were in close absorbance with those of the Yousefi N et al. (24).

3.5. Kinetic and Isotherm Investigations

To percept the dynamics of the adsorption reaction, data can be analyzed by the adsorption kinetics. In the current study, to achieve these goals, the 1st and 2nd order kinetics were investigated. According to the obtained results, the mean of correlation coefficient (R^2) in the 2nd-order kinetic model was higher than that of the 1st-order kinetic model. Therefore, the experimental data showed that the adsorption of reactive red 198 on both active carbon and graphene fitted well the 2nd-order kinetic model (Figures 6 to 8). The pseudo-second-order hypothesizes that 2 reactions affect the adsorption of pollutants in parallel: the 1st one was fast and reached the equilibrium time and the 2nd one had a lower rate and continued for longer time.

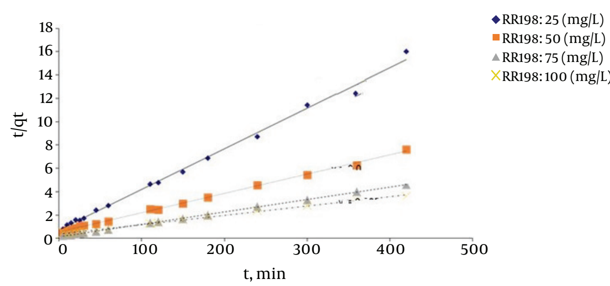

Figure 6. Second-Order Kinetics of Reactive Red 198 Adsorption on Activated Carbon

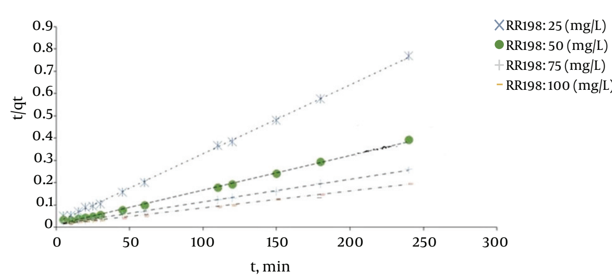

Figure 7. Second-Order Kinetics of Reactive Red 198 Adsorption on Grapheme

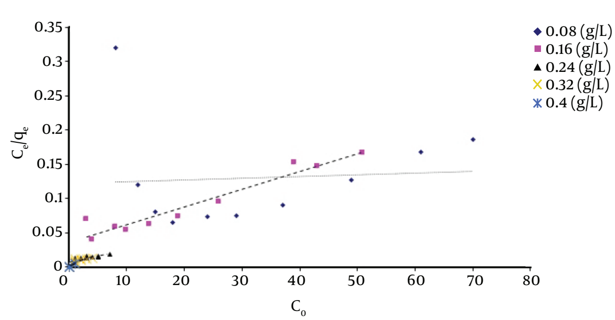

Figure 8. Langmuir Isotherm for Reactive Red 198 Adsorption on Activated Carbon

Adsorption is an equilibrium separation process (27). The parameters of adsorption isotherm present information on the adsorption capacity of adsorbents (28). Constant and special amounts in isotherm show the properties of surface and adsorbent dependency and can be used to compare the adsorption capacity of adsorbents in removing contaminants (29). In the current study, isotherms of Langmuir 1, 2, and 3 and Freundlich were investigated; the data showed that the adsorption isotherm of reactive

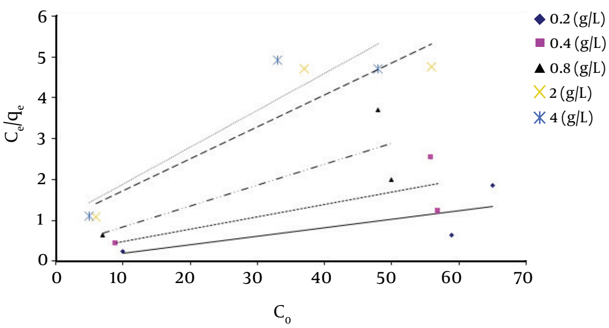

Figure 9. Langmuir Isotherm for Reactive Red 198 Adsorption on Activated Graphene

red 198 on the adsorbent: active carbon and graphene fitted well the Langmuir model, considering higher amounts of regression; this illustrates that the process is homogeneous and monolayer adsorption.

4. Conclusion

The current study investigated the adsorption of reactive dye and reactive red 189 on active carbon and graphene, and the effects of different variables including initial dye concentration, pH, contact time, and different doses of the adsorbents; the main findings were as follows:

- The efficiency is entirely dependent on pH; the highest removal efficiency for both adsorbents happened at pH value of 3.

- Using graphene, the time to reach adsorption equilibrium was faster. It can be noted that this adsorbent can effectively remove the dye from aqueous environments at lower contact time.

- The adsorption efficiency increased with increasing the amounts of both of the adsorbents.

Since a lower amount of graphene is required for the maximum removal efficiency, this adsorbent is preferred to activate carbon and it is also cost-effective. Moreover, the graphene efficiency in adsorption of reactive red 198 in all studied concentrations of the dye was in the range of 98% to 100%; this can be considered as a special feature of graphene adsorbent in removing pollutants.

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