Natural Nanoporous Filter Material as a New High-Efficiency Natural Adsorbent to Remove Textile Dyes

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Abstract

The objective of this paper is to perform the innovation design of removing most textile dyes that are harmful to the environment and might induce cancer. However, many methodologies had been developed for various chemical and physical processes to remove different dyes, such as ozone oxidation, electrochemical methods, chemical coagulation, hypochlorite oxidation, and adsorption to remove dyes from wastewater. A novel nanoporous filter methodology and mathematic simulations for adsorption were established as an effective medium for removing dyes from wastewater which was compared to other expensive treatments. The different concentrations of the dye liquid are used as a tester, and the different concentrations of nanoporous adsorbent were added in a uniform distribution and were tested with different time courses and under different temperatures. The final readings were measured by a spectrophotometer and fit into a mathematic model. The result indicates that this nanoporous and natural adsorbents are very good at cleaning the dyes in this system. The fit-in mathematic models could be applied in these tests which can be used in the industrial conditions for a low cost without secondary dye pollutions.

Keywords: natural nanoporous filter, textile wastewater, adsorption test, mathematic simulation model

1. Introduction

Most of the ready-to-wear market and the pursuit of fashion in today's society have resulted in large garment factories around the world that use large amounts of water, chemicals, dyes, etc. These factories will produce a large amount of wastewater. If they didn’t discharge into the river or the sea, they would directly cause environmental pollution. Indirectly, they would affect human health and even death due to bioaccumulation [1-4].

Dyes are aromatic molecular structures that are expected to be strong and stable. Therefore, they are difficult to degrade (making them more difficult to biodegrade). They are very toxic and harmful, however, they may cause a large amount of environmentally toxic waste or pose a serious hazard to public health. Scientists have developed various chemical and physical processes to remove different dyes. For example, dyes are removed from wastewater by ozone oxidation, chemical coagulation, electrochemical methods, hypochlorite oxidation, and adsorption [2, 5-8].

Adsorption is an effective method for removing dyes from wastewater, and it is an alternative to other expensive processing techniques. Some studies in the literature have reported the use of natural adsorbents to remove textile dyes because of their economic appeal and advantages, primarily because they are inexpensive and available. However, we need to find effective natural adsorbents with high adsorption capacity. Furthermore, they can be easily separated and set up standard procedures for recycling and regeneration [6, 9-11].

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Among natural materials, natural clay minerals are ideal adsorbents due to their low cost, abundant resources, strong adsorption, and ion exchange capacity. The adsorption capacity of these clay minerals is derived from the negative charge of their surface structure and can adsorb positively charged ions in the sewage. The adsorption performance is produced by a large specific surface area and a good porosity. An in-depth study of the interaction between pollutants and clay particles is needed, such as bentonite and diatomaceous earth. Clay minerals are effective in adsorbing inorganic and organic pollutants. The most widely used adsorbents for wastewater is activated carbon because of its high removal capacity. However, its use is subject to regeneration problems, high-cost production, phase separation difficulties, and poor mechanical properties [7, 12].

The natural nano-composite filter is a kind of natural mineral, which is obtained by washing with sulfuric acid and baking at high temperatures. It can be processed into particles. For example, adding natural adhesive can make the mineral powder into filter particles of smoke. The manufacture of natural nano-composite filter material is from a variety of mineral flour with the specific proportion of ore combination, and their inside appearances are like a sponge structure with many nano-sized pores, which increased its adsorption capacity [13]. The production procedure of this natural nano-composite is simpler than activated carbon, so the cost is lower twice than functional activated carbon. Because it is made of natural mineral powder, it would not cause the second pollution into the environment.

This study focuses on the experimental conditions of nano-composite adsorbent with different dyes in different rpm (shaking speed), ppm (solute dye concentration). Moreover, this study would investigate the formula in which their characteristics of dye-binding and their emission requirements by the selection of appropriate treatment methods such as the effects of binding time, different dye concentrations, different shaking speeds. The dyes in this study were methylene blue (MB) and Cationic dyestuffs No. 257 black (BD). MB is commonly used in absorption test, while the BD dye does not contain acidic groups and exhibits catholicity in water, also known as cationic dyes.

2. Materials and Methods

2.1. Preparation of adsorbent

The Natural nano-composite filter is powdered and requires a water wash step for the accuracy of the experimental data. Washing step, take 10 g nano-composite filter in a 50 ml centrifuge tube and add 40 ml of distilled water, mix well, centrifuge for 5 minutes (3000 rpm, 25°C), pour off the supernatant, add 10 ml. The distilled water was then poured into a glass petri dish and finally baked overnight (90°C) in an oven.

2.2. Dye solution preparation

In this study, the cationic dye “methylene blue” was selected as the control group; the cationic dye “cationic dyestuffs No. 257 black” was selected as the control group to compare the practicability of the nano-composite filter. A stock solution having a concentration of 1000 ppm has been obtained by dissolving a precisely weighed dye sample in distilled water. The dye stock solution (1000 ppm) was diluted with distilled water to the desired concentration, while other concentrations were required. All solutions were not subjected to any pH adjustment. The chart of Figs. 1(a) and 1(b) showed the full length scanning of these two dyes, and in the chart that showed the unit of the Y axis as OD reading, and the unit of the X-axis as nm.

2.3. Adsorption balance time

Weigh 1g washed with water nano-composite filter placed in 50 ml centrifuge tube and then added 50 ml 300 ppm concentration of the dye solution, mixed well, the use of 125rpm operation of the temperature control vibrator bottle placed at 25 ± 2°C, the sampling interval at different times from the shaker. After centrifugation (3000 rpm, 25°C, 5 min), the residual
concentration of the dye solution was measured using an ELISA at a wavelength of 660 nm (methylene blue) and 600 nm (cationic dyestuffs No. 257 black), respectively (Figs. 2(a) and 2(b)).

2.4. **Effect of different concentrations on adsorption**

Add 300 ppm dye solution to a series of 50 ml centrifuge tubes, add 1 g nano-composite filter, mix well, and place the bottle at 25°C, 30°C, 35°C using a temperature-controlled vibrator operating at 125 rpm. C, 40°C, 45°C, 50°C, 55°C, shaking for 3 h. After centrifugation (3000 rpm, 25°C, 5 min), the absorbance of the dye solution was measured at 660 nm and 610 nm using an ELISA, respectively.

2.5. **Effect of different temperatures on adsorption**

Add 300 ppm dye solution to a series of 50 ml centrifuge tubes, add 1 g nano-composite filter, mix well, and place the bottle at 25°C, 30°C, 35°C using a temperature-controlled vibrator operating at 125 rpm. C, 40°C, 45°C, 50°C, 55°C, shaking for 3 h. After centrifugation (3000 rpm, 25°C, 5 min), the absorbance of the dye solution was measured at 660 nm and 610 nm using an ELISA, respectively.

2.6. **Effect of different RPM on adsorption**

Add 300 ppm dye solution to a series of 50 ml centrifuge tubes, add 1 g nano-composite filter, mix well, and place the bottle at 25°C, 30°C using a temperature-controlled vibrator operating at 100 rpm, 125 rpm, 150 rpm. C, 35°C, 40°C, 45°C, 50°C, 55°C, shaking for 3 h. After centrifugation (3000 rpm, 25°C, 5 min), the absorbance of the dye solution was measured at 660 nm and 610 nm using an ELISA, respectively.
2.7. Adsorption kinetics

Adsorption kinetics is the main method to explore the adsorbent adsorption machine. The kinetic models for adsorption are Pseudo-First Order and Pseudo-Second Order. The expressions are:

(1) Pseudo-First Order

$$\ln\left(1 - \frac{q_t}{q_e}\right) = -k_1t$$

(2) Pseudo-Second Order

$$\frac{1}{q_t - q_e} = k_2 + \frac{1}{q_e}$$

where $q_t$ is the adsorption amount per unit mass of adsorbent at time $t$ (mg/g), $q_e$ is the adsorption amount of adsorption equilibrium adsorbent (mg/g), $k_1$ is the adsorption rate constant of the pseudo-first-order equation kinetic model (min$^{-1}$), and $k_2$ is the adsorption rate constant of the quasi-second-order equation dynamics model (g · mg$^{-1}$ · min$^{-1}$) [14-17].

3. Results and Discussion

3.1. Dye full-length scanning chart

The following charts were the full-length visible light scanning of the two dyes at 660 nm (Methylene blue, MB) and 610 nm (Cationic dyestuffs No. 257 black, BD). The charts showed the lambda max of the two dyes from full wavelength scanning (Visible wavelength: 380 nm - 700 nm). The following experimental results for the control group of distilled water, the absorbance reading is 0.0393.

3.2. Adsorption balance time

According to Fig. 2(a), the absorbance of the supernatant decreases with time and tends to be constant after 3 h. The results showed that at room temperature nano-composite filter adsorbed about 3 h equilibrium, and the following experiment selected 3 h adsorption equilibrium times.

3.3. Effect of different concentrations on adsorption

According to Fig. 3, the adsorption effects of different concentrations were determined under fixed RPM. The three images clearly show that the BD is almost completely absorbed in the concentration of 400 ppm at 100 ppm, and the supernatant can be completely clarified after 3 h; the concentration is 600 ppm, and the supernatant cannot be clarified after 3 h of adsorption equilibrium time.

![Fig. 3 Adsorption effect at different concentrations of BD](image-url)
According to Fig. 3, the adsorption effect at different concentrations of BD can be clarified after adsorption. The data shows that the maximum adsorption concentration of the material for MB is below 550 ppm.

3.4. Effect of different RPM on adsorption

According to Fig. 4, the adsorption concentration of MB concentration of 300 ppm and 350 ppm can be clarified after adsorption. The data shows that the maximum adsorption concentration of the material for MB is below 550 ppm.

According to Fig. 5, the adsorption effect of the same concentration of BD under different RPMs is shown. Several data showed that 125 rpm is better than 150 rpm. For this result, because a larger rpm will be studied later, the reason will be discussed after the data comes out.

According to Fig. 6, the adsorption effect of the same concentration of MB at different RPMs is shown. The results at a concentration of 300 ppm to 350 ppm showed that the effect of 150 rpm was better than that of 125 rpm; the concentration of 400 ppm - 500 ppm showed that the effect of 125 rpm was better than 150 rpm. For this result, because a larger rpm will be studied later, the reason will be discussed after the data comes out.
Fig. 5 Adsorption effects at different rpm

Fig. 6 The adsorption effect at different rpm
3.5. Adsorption kinetics

Finally, insert the Pseudo-Second Order. The formula for the two dyes is shown in Table 1. The formula quantifies the amount of adsorption.

| Cationic dyestuffs No.257 black (BD) | \( K_2 (g \cdot mg^{-1} \cdot min^{-1}) \) | \( q_e (mg/g) \) |
|-------------------------------------|----------------|----------------|
| Methylene blue (MB)                 | 2.157x10^{-1}  | 4.523          |
|                                     | 2.310x10^{-1}  | 2.643          |

4. Conclusions

The obtained shows that the commercially available natural nanoporous filter material in this study leaves dye-polluted wastewater 100% dye-free.

To reach the dye-free condition for methylene blue our study shows that the ideal set of variables is a concentration of up to 550 ppm at 25°C and a shaking speed at 100 rpm for 3 hours.

To reach the dye-free condition for Cationic dyestuffs No. 257 black (BD) the optimum adsorption condition is a concentration of 550 ppm at 45°C and a shaking speed at 150 rpm for 3 hours.

Besides, using pseudo-second-order adsorption kinetics, we created a 3-parameter model to design a schedule of nano-composite concentrations for different scales of application. These formula parameters will enable the industry to apply the findings to a range of production scales at the lowest cost and with no secondary pollutions.

Conflicts of Interest

The authors declare no conflict of interest.
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