



Bisorption of Rhodamine-B dye by native and acid- activated orange peel as low-cost adsorbent

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Abstract

In this work, the removal of Rhodamine-B dye from aqueous solutions by adsorption on native and activated carbon prepared by chemical activation using HNO_3 for orange peel was examined. The results showed that activating the activation and carbonization of the adsorbents rises the existence of carbon pores. The adsorption experiments were done by using several rates of initial pH, adsorbent dosage, contact time and initial concentration of the adsorbate for the raw and activated adsorbent. The greatest percentage removal of Rhodamine-B dye by orange peel (OP) and activated orange peel (AOP) was found to be 84% and 98% respectively. Langmuir and Freundlich isotherms were used to study the equilibrium results. The experimental results fitted good to the Freundlich isotherm. The results established that both (OP) and (AOP) was highly effective as adsorbents in the removal of Rhodamine-B dye.

Keywords: Rhodamine-B, Orange peel, activation, Adsorption

Introduction

The discarding of waste-water from several industries, like textile, paper, plastics, leather, food, and cosmetics, takes special interest by scientists. These wastes contain a diversity of toxins like heavy metals, coloring material, and organic pollutants. One of the most significant of these toxins is dye substances. Different industries produce large volumes of dye including wastes, such as textiles, paper, rubber, leather, cosmetics, and food industries. The removal of these colored wastewaters without suitable treatment into aquatic bodies will harmfully influence the natural aquatic environment as well as have carcinogenic and mutagenic impressions on human beings ^[1,2]. To remove the dyes in industrial water sewages chemical, physical, and biological methods such as extraction, chemical oxidation, microbiological decomposition, ion exchange, photocatalytic degradation, adsorption on activated carbon, combined of adsorption and degradation and ultrasonic decomposition were concerned with highly economical ^[3]. The adsorption process by agriculture wastes used a new, inexpensive and accurate technique for removal of unlike toxins, similar application of bio-adsorbent particularly based on non-toxic and ecological with high surface area and active sites is a great requirement ^[4]. Presently, there is increasing importance to use lesser price, as well as commercially accessible materials, have been selected for the adsorption of dyes. A varied number of articles are found in literature for the preparation of activated carbons by acid activation means from cheaper and readily accessible materials like Juniperus (JH) and Solenostemma Argel (Del) Hayne (SH) ^[5], Rice husk (RH) and rice stalk (RS) ^[6] and barely husk ^[7]. In this paper, the adsorption of widely used Rhodamine-B dye has been studied. Rhodamine B is a chemical compound and a dye. It is often spent as a tracer dye in the water to determine the level and direction of movement and transport. Rhodamine dyes fluoresce and can thus be discovered simply and cheaply with fluorometers. Rhodamine dyes are used widely in biotechnology applications such as

fluorescence microscopy, flow cytometry, fluorescence correlation spectroscopy. Rhodamine-B is distrusted to be toxic and thus produces having it must enclose a threatening on its label ^[8]. Thus their removal in an eco-friendly way is studied here, by the utilization of orange peel as a low-cost adsorbent.

Materials and methods

Preparation of the adsorbent

Orange peel(OP) expended in this work was gained from agricultural fields in Egypt. (OP) was washed with distilled water to eliminate dust and impurities, then dried at room temperature for two days. Finally crushed, grinded and sieved. Chemical modification of these adsorbents was carried out through carbonization and activation. Adsorbents were carbonized by putting it in an electric muffle furnace, which was then heated in the absence of oxygen at a temperature of 300°C - 700°C for one hour. Samples of all the carbonized material were saturated in one mole from concentrated nitric acid (HNO_3). The materials were then removed from acid after the 24 hours and then washed with distilled water until all impurities caused by free acid were removed. Lastly, the Adsorbents were dried in a furnace at 60°C for an extra 4 hours.

Preparation of the stock dye solution

The stock solution of synthetic dye Rhodamine-B (RB) was prepared by dissolving 0.5 g of dyes in distilled water and making it up to 100 ml in a standard flask. Dye concentration was concluded by using absorbance values considered before and after the handling, (Spectro UV-Vis Double Beam UVD-3500, Labomed spectrophotometer was used. The wavelength of maximum absorbance attained to be 550 nm. RB was obtained from Merck Chemicals, UK. The chemical structure of RB dye is shown in Figure 1.

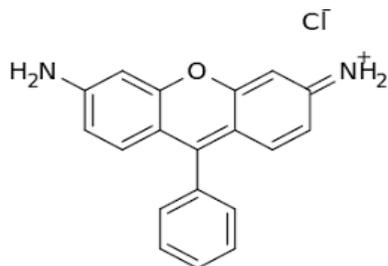


Fig 1: structural formula of Rhodamine-B dye (RB).

Characterization Methods.

The surface morphology of (OP) and (AOP) was established using scanning electron microscopy (SEM).

Adsorption experiment

The batch investigations were carried out in a series of conical flask (250mL) where the solution of Rhodamine-B (RB) dye (50mL) with different concentrations. The pH adjusted by 0.1M of hydrochloric acid and 0.1 sodium hydroxide. 0.5 g from (OP) and (AOP) separately were added to dye solution and specified in constant stirring for 30min to reach equilibrium. The mixture was then centrifuged and the supernatant concentration recognized. Several factors that influence the adsorption process were experimented by adsorbent dosages (0.2-1.0 g), initial pH of the solution (2-12), contact time (5-60 min) and initial concentration (10-100 mg/L). All experiments were performed at room temperature. The removal efficiency and the equilibrium

uptake of dyes were supposed matching to the equations (1, 2) (9):

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$\% q_e = \frac{C_0 - C_e}{M} \times V \quad (2)$$

Where, C_0 is the initial concentration of dye (mg/L), C_e is the equilibrium concentration (mg/L), q_e is the amount of adsorbed dye in mg/g, M (g) weight of the adsorbent and V volume of solution in liters.

Results and Discussion

Characterization of the adsorbent

Scanning Electron Microscopy (SEM) is generally used to report the morphological structures and surface descriptions of adsorbent materials. The surface morphology of (OP) and (AOP) was observed using Scanning Electron Microscopy (SEM) and the results are shown in Figure 2. As seen in Figure 2 SEM image for (a) (OP) (b) (AOP) shows ordered surface, porosity, gaps and cavern type openings on the outside of the activated carbon (10). Activated carbons prepared from cellulosic materials are widely used as adsorbent due to their high adsorption capacity, high surface area, microporous structure and a high degree of surface adsorption. The chemical nature and pore structure usually determine the sorption activity [11].

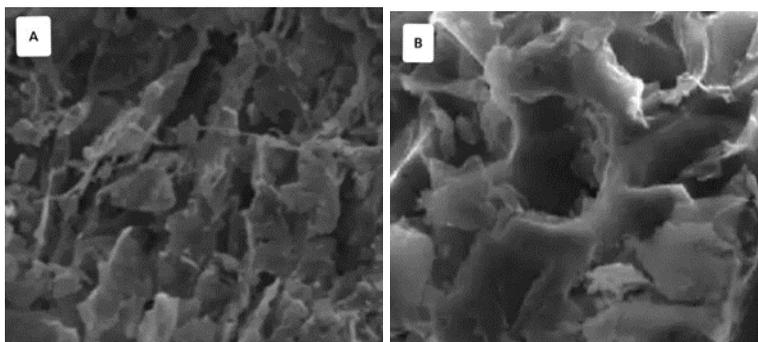


Fig 2: SEM micrograph of (A) OP (B) AOP.

Effect of Initial pH

The pH of the dye solution is a considerable aspect that influences the adsorption ability. Figure 3 shows the maximum percentage removal of Rhodamine-B (RB) by using (OP) and (AOP) was obtained when the pH 8. The pH value influences the structural immovability of the Rhodamine-B molecule. The results indicate that the adsorption of Rhodamine-B increase with decrease the acidity that is for the reason that in the acid medium the hydrogen ion matched with Rhodamine-B dye molecule and as the number of hydrogen ion decreased more adsorption site will be free to adsorb Rhodamine-B dye (12).

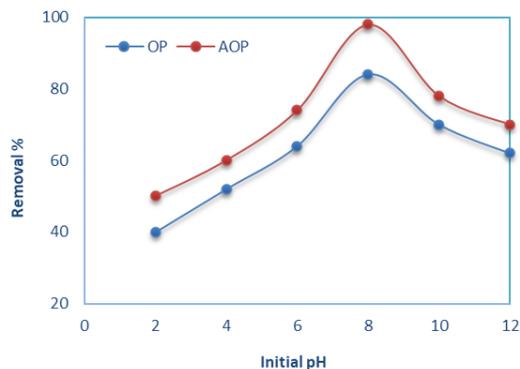


Fig 3: Effect of initial pH of dye solution using (OP) and (AOP) on removal of Rhodamine-B (RB) from aqueous solutions.

Effect of adsorbent dosage

The effect of the different weights of the (OP) and (AOP) on Rhodamine-B (RB) removal was considered by varying the adsorbent weight from 0.2g to 1g at pH 8. Figure 4 shows that dye removal increases with an increase in the weight of all adsorbents. The adsorption percent increase with the increase in the adsorbent dosage, this is because the surface area is greater, which means a greater number of adsorbent sites (13).

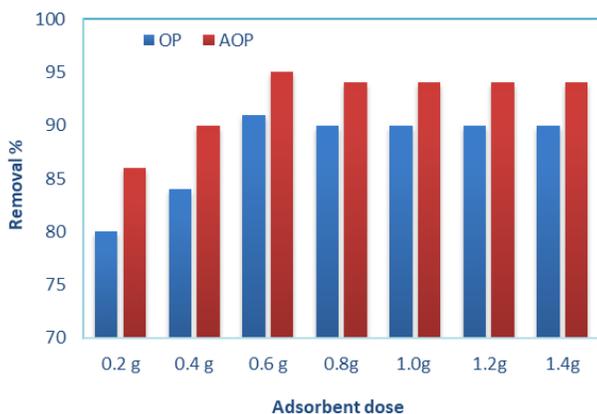


Fig 4: Effect of adsorbent dosage (g) of (OP) and (AOP) on removal of Rhodamine-B (RB) dye from aqueous solutions.

Effect of initial dye concentration

The effect of various initial dye concentrations is examined at (10-100 mg/L) holding the adsorbent dose at 0.5 g/L. Figure 5 shows that the maximum adsorption of dye was at concentrations of 10 and 20 mg/L. The results show that adsorption percent decreased with the increase of the initial dye concentration. At a low concentration of dye, the ratio of surface active sites for total dye is high. Therefore, the dye ions could interrelate with the Sorbent to occupy the active sites on the carbon surface sufficient and can be removed from the solution, but with the increase in dye concentration, the number of active adsorption sites is not enough to acclimate dye ions (14).

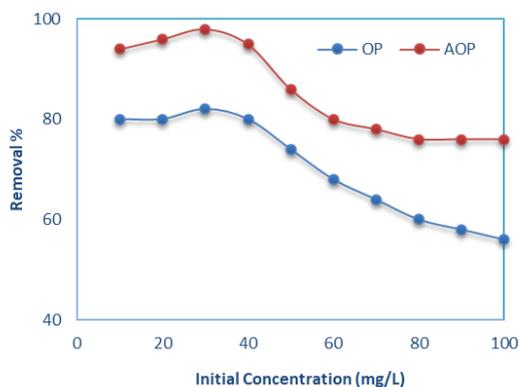


Fig 5: Effect of initial Rhodamine-B (RB) dye concentration on the removal percent

Effect of contact time

The removal of Rhodamine-B (RB) dye by adsorption on (OP) and (AOP) was studied as a function of contact time, and percentage removal plotted against time. Figure 6 shows the

adsorption rate of Rhodamine-B onto all forms of adsorbents is fast at the beginning and becomes constant after 30 min. The removal percent decreased to a constant value with an increase in contact time due to all available sites were covered and no active site accessible for further binding of dye molecules to the adsorbent surface. A great number of unfilled surface sites are accessible for adsorption initially and after some time, the remaining unfilled surface sites are difficult to be conquered due to repulsive forces between the solute molecules on the solid and bulk phase solution (15).

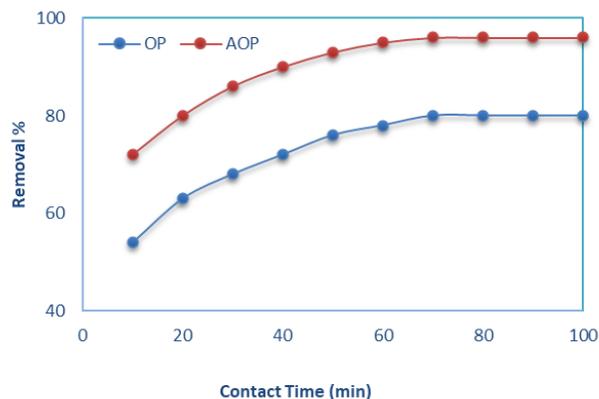


Fig 6: Effect of contact time on the removal percent for Rhodamine-B dye (RB).

Adsorption Isotherm

The adsorption isotherms are fundamental essentials for analyzing any adsorption system. The experimental data were set to Langmuir, Freundlich and Temkin isotherms. The Langmuir equation, which is working for monolayer sorption into a homogeneous surface with a controlled number of identical sites, is given by equation (3) (16):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3)$$

Where C_e (mg/L) dye concentration at equilibrium, q_e (mg/g) equilibrium uptake, and q_m , K_L are Langmuir constants.

The Freundlich model is the first known relationship describing the sorption equilibrium and is specified by equation (4) below (17):

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (4)$$

Where C_e (mg/L) dyes concentration at equilibrium, q_e (mg/g) equilibrium uptake, k_F and n are Freundlich constant.

Temkin isotherm is supposed that the heat of adsorption decreases linearly with increasing coverage and is stated by equation (5) below (18):

$$Q_e = B_T \ln K_T + B_T \ln C_e \quad (5)$$

Where, K_T is the equilibrium binding constant (L/mg), B_T is the variation of the adsorption energy (KJ/mol). The isotherm constants and R^2 values are in table 2. showed that the Freundlich

isotherm is greater than obtained by Langmuir and Temkin isotherm, demonstrating the applicability of this model more better than Langmuir and Temkin one. It means that the multi-layer physical adsorption of all dye molecules on these adsorbents. The good agreement of Freundlich isotherm indicates also that the surface of the activated carbon prepared from OP and AOP is highly heterogeneous (18).

Table 1: Equilibrium isotherm constants for Rhodamine-B (RB) dye adsorption onto different adsorbents at room temperature.

Adsorbent	Langmuir			Freundlich			Temkin		
	q_m	K_L	R^2	n	K_F	R^2	B_T	K_T	R^2
OP	6.277	0.094	0.985	2.475	1.208	0.997	1.379	1.415	0.964
AOP	6.997	0.106	0.980	2.238	1.085	0.998	1.293	1.123	0.973

Conclusion

The data reached from the present article determined that activated carbon prepared from OP and AOP was excellent and effective adsorbent for the removal of Rhodamine-B (RB) dye from aqueous solution. The factors affecting the adsorption rate such as contact time, initial dye concentration, temperature, etc. were optimized. The equilibrium results were analyzed using several adsorption isotherm models. Langmuir, Freundlich and Temkin isotherms were used to study the equilibrium results. The experimental results fitted good to the Freundlich isotherm. Thus, the present study has shown that OP and AOP could be used as an effective adsorbent for the removal of Rhodamine-B (RB) dye from aqueous solution, with higher in effectiveness for AOP better than OP.

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