



The Adsorptive Acid Orange 7 using Kenya tea Pulps Ash from Aqueous Environments

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Abstract

The control of environmental pollutions specially water resource pollutions is one of the main challenges throughout the world. The discharge of industrial wastewater such as textile industries containing toxic dyes like acid orange 7 has added to this concern. In this research, the adsorption of acid orange 7 anionic dye on the raw fine-grained tea waste modified with an acid and calcined has been investigated through the adsorption method. To achieve this purpose, the adsorbents of fine-grained CTC tea waste were studied in three forms of raw, treated with concentrated phosphoric acid, and calcined at 350, 450, and 500 °C for the adsorption of acid orange 7 with 50-500 mg/L concentrations from the aqueous conditions at pH 2-10 and t 0-120 min using 1-10 g/L adsorbents. The results showed that the best removal yield is about 98% at pH 2 and time 120 using 50 mg/L of dye and 10 g/L of adsorbent, and the modifications have a negligible effect on the improvement of the raw fine-grained tea waste adsorption. The most adsorption capacity (41.66 mg of orange 7 dye) was obtained using 1 g of the adsorbent. Also, the results illustrated that the adsorption pattern is in agreement with the Langmuir and Freundlich isotherm models. The adsorption pattern in the Freundlich model (R^2 97%) is slightly more than Langmuir model (R^2 85%). According to the granulated structure of tea waste (fine-grained tea) in three forms of raw, acidic and calcined, Kenya is an appropriate and low-cost adsorbent in the adsorption of orange 7 dye from the aqueous media.

Keywords: Water pollution, Adsorption, Kenya tea waste, Acid orange 7 dye

Introduction

The control of environmental pollutions especially the water resources pollutions is one of the main challenges of researchers around the world (1-3). The discharge of industrial wastewaters containing the dyes in the fertilizer, paper, rubber, plastics, leather, pharmacy and health industries is a serious problem of environmental protections (4-6).

The discharge of colored wastewaters without a suitable treatment of aqueous ecosystems has damaging effects such as the decrease of light transmission and photosynthesis (7, 8). In addition, the dyes have the carcinogenic and mutagenic effects due to the presence of aromatic rings in their structures, and threaten the human and animal lives (9). The dyes are resistant to the light, oxidation, and aerobic and biological treatments, and treatment of the wastewaters polluted with these compounds is very difficult (10, 11).

Until now, different processes such as the adsorption, electrochemical coagulation, oxidation, chemical precipitation, aerobic treatment, flotation and ion exchange have been reported for the removal of dyes from the aqueous solutions (12-14). Among these processes, the adsorption is an environmentally friendly, simple and economic method in the wastewater treatment (14).

The tea waste is a low-cost, natural and available adsorbent, and in some research, it has been applied in the forms modified with the water, acid, base, and carbon for the removal of pollutants (15). In a study, the magnetic nanoparticles stabilized on the tea waste were used for the removal of Cr(VI) and Cu (16, 17). In 2015, Borah *et al.* performed the activated carbon prepared from the tea waste to remove the cationic and anionic dyes, and reported the removal yield more than 99% at neutral pH (18).

Also, in 2015, Foroughi Dahr *et al.*, investigated adsorbing the red color of Congo by the tea waste modified with the surfactants (19). In another research, in

2014, Pirbazari *et al.* applied the tea waste treated with NaOH to remove the methylene blue from aqueous solutions (20). Although the activated carbon has a good efficiency for the removal of pollutants, the carbon adsorbents are costly and their revival and burial are difficult (19).

The polluted wastewaters yearly enter 7×10^5 tons of color into the aqueous ecosystems. Among the synthesized dyes, the acidic dyes have been performed due to their solubility in the water. The orange 7 is an acidic dye which is highly toxic and carcinogenic, and damages the eyes and skin (21). Therefore, in this research, the ability of CTC tea waste (fine-grained) in the removal of acid orange 7 from the aqueous solutions *via* the adsorption method has been studied.

Materials and Methods

The dye used in this research with the commercial name of acid orange 7 (orange II) is an acidic dye and has widely been used in the paper and textile industries (22). Since the maximum absorption wavelength orange 7 is in the visible area at 483 nm, this wavelength was used for the characterization of compounds in the aqueous solutions *via* the UV-Vis spectrophotometer. To prepare the adsorbent, first, the fine-grained tea waste (ant's head) was used in three forms of raw, treated with phosphoric acid in the proportion of 3:1, and calcined at 350, 450, and 500 °C for the removal of dyes.

The adsorption tests: A 1000 mg/L of acid orange 7 solution was prepared using the distilled water, and the desired concentrations (50, 100, 150, 200, ..., and 500 mg/L) were prepared. Then, the effects of pH and adsorbent amounts on the adsorption process were investigated to obtain the highest adsorption yield. The solutions' pH was adjusted in the range of 2 to 10 using 0.1 M nitric acid and 0.1 M sodium hydroxide. After setting the test conditions, 10 g of adsorbent were added to a solution (1000 mL) containing the specified concentrations of the dye, and the mixture

was put on the shaker (100 rpm) for 120 min. After 120 min, the samples were filtered using a 42 μm Whatman filter paper, and the concentration of the dye remained in the solution was measured at the wavelength of 483 nm using a UV-Vis spectrophotometer. The removal percent was calculated using Eq 1.

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

Where C_0 is the dye initial concentration and C_f is the concentration of remained dye after the adsorption process (23).

Results and Discussion

The Effects of Different Modifications on the Adsorption Process using the Tea Waste

The effects of raw adsorbent, and the adsorbent modified with an acid and calcined at different temperatures on the dye adsorption using the fine-grained tea waste have been demonstrated in Fig 1. The biosorbents calcination not only increases the adsorbents surface but also changes the acidic properties of adsorbents to the basic properties (24). In this study, the adsorbent calcination results in the more porous structure of the grained tea waste which plays an important role in the dye adsorption.

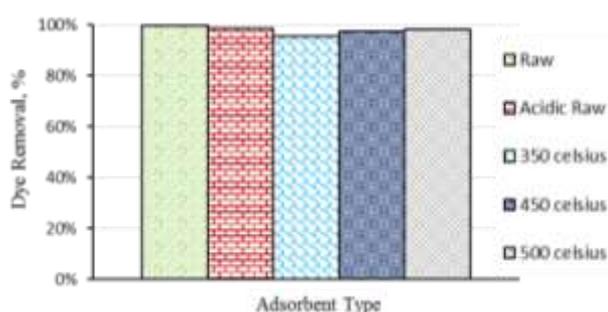


Fig 1: The effects of different modifications of adsorption on the removal AO7 dye (50 mg/L dye concentration, pH 2, and t 120 min)

Investigating different studies depicts that the carbon prepared from the tea waste increases the dye adsorption in the presence of an activator agent. In the mentioned research, phosphoric acid was used as an activator agent in the preparation of activated carbon from the tea, and good removal yields were achieved in the

pollutants removal (18). In another study, potassium carbonate (K_2CO_3) was used to prepare the activated carbon from the tea. Also, the potassium acetate was performed in the preparation of the activated carbon from the tea to remove the methylene blue dye (15).

However, in this research, the temperature without the calcination process was used, and the results showed that this action does not have an effect on the improvement of removal yields. In the study, the calcination of rice bran at 600 and 800 $^\circ\text{C}$ decreases the adsorption capacity in comparison with the raw samples, and the adsorption capacity was increased at 1000 $^\circ\text{C}$.

The results of this research illustrated that the amount of adsorbed dye depends on the physical properties of adsorbent (special surface and the diameter average of pores). The adsorbent surface plays an important role in the dye removal (25), and produces tiny pores in the preparation of CTC fine-grained tea (26). The acidic modification improves the physical and chemical properties and morphology of adsorbents, and increases the dye adsorption (27). In current research, acidic modification did not have an effect on the removal under the desired conditions. As depicted in Scheme 2, the acidic and thermal modification did not affect the dye adsorption using the tea waste.

However, in all cases, the removal yields were more than 90%. Moreover, the unmodified tea waste is more affordable than the calcined and acidic modified samples. Therefore, the raw tea waste was used in the following steps.

The pH Effects on the Adsorption using the Tea Waste

The pH is one of the main parameters in the adsorption process. The effects of pH on the orange 7 adsorption in the 50 mg/L concentration of dye using 10 g/L adsorbent have been shown in Fig 2. The results depicted that the orange 7 adsorption by the tea waste is independent from the pH. In this research, very little changes were observed in the adsorption by varying pH parameter.

The most adsorption was obtained at pH 2, and increasing pH decreases the adsorption. This can be due to the changes of ionization in the solution and also ionization of functional groups on the adsorbent surface by varying the charge of its surface. The sulfonate group of acidic orange 7 is dionized in the water, and creates the ionic form of its molecule. On the other hand, increasing pH raises the negative charge of the adsorbent, and repulsive forces prevent the acid orange adsorption (28).

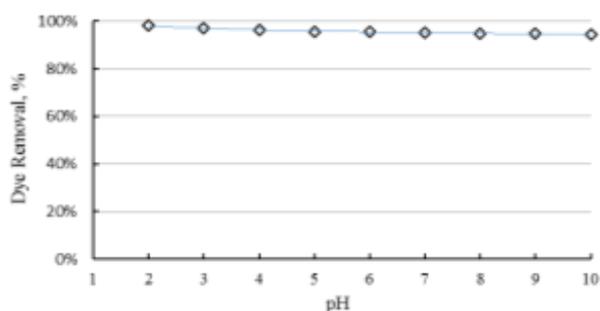


Fig 2: The effects of initial pH on the orange II dye adsorption using the tea waste (50 mg/L dye concentration and t 120 min)

The Effects of Dye Initial Concentration

Changing initial concentration varies the motive force in all reactions. The effects of changes of dye initial concentration on the adsorption using the tea waste were investigated in the range of 50-500 mg/L (Fig 3).

In the range of 50-100 mg/L, the 90-98% removal yields were obtained while in higher concentrations, the adsorption decreases and reaches the 72% yield in 500 mg/L concentration. In higher concentrations, the molecules compete together to achieve the adsorption sites so it decreases the adsorption amount (21).

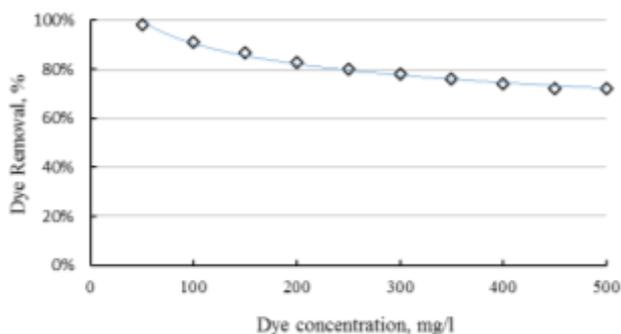


Fig 3: The effects of changes of orange 7 initial concentration on the dye adsorption (pH 2 and t 120 min)

The Effects of Time

Investigating the optimum contact time for the acid orange adsorption at pH 2 in the concentration of 50 mg/L has been depicted in Fig 4. In the first 5 min, more than 92% dye were removed, and the increase of contact time to more than 45 min did not have a great impact on the adsorption. The high adsorption in initial steps is due to the presence of adsorption sites unoccupied on the adsorbent's surface. After the occupation of adsorption sites, due to the repulsive forces between the adsorbed molecules, the unoccupied sites are barely able to adsorb more dyes. The similar results have been obtained for the dye removal using biomass alga (11), and carbon nanotubes (29).

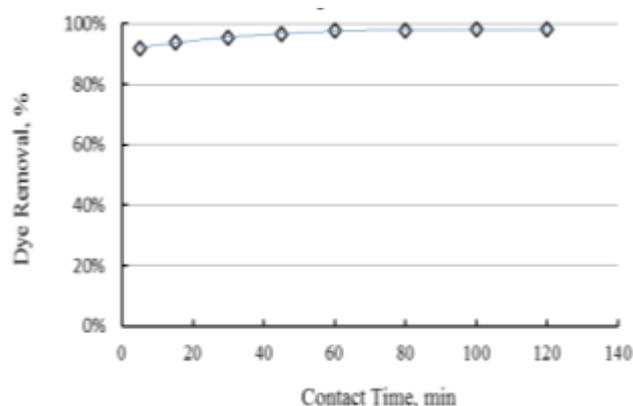


Fig 4: The effects of contact time on the orange 7 dye adsorption (50 mg/L dye concentration and pH 2)

Adsorption Isotherm

The adsorption equilibrium is usually characterized as an adsorption isotherm at specific temperatures which is a good way for choosing the best adsorbent and predicting adsorption system efficiency (22). The Langmuir and Freundlich isotherm models are usually performed for the adsorption equilibriums. The Freundlich isotherm, which has experimentally been obtained, is defined by the following Eq:

$$\frac{x}{m} = K_f C_e^{1/n} \quad \text{Eq (2)}$$

Where x/m (or q_e) is the amount of adsorbed compound per the adsorbent's weight and C_e is the equilibrium concentration of the adsorbed compound after the adsorption process. K_f and n are the experimental constants of the equation. K_f is the adsorption capacity and n shows the energy or the adsorption intensity.

The Freundlich isotherm is the most significant multiple adsorption isotherm for the heterogeneous surfaces (30). If $n = 1$, the adsorption process is linear, and it shows that the adsorption sites are in the homogeneous energy, and no reaction occurs between the adsorbed molecules. If $(1/n) < 1$, the adsorption is suitable, the adsorption capacity increases, and new adsorption sites are created.

If $(1/n) < 1$, the adsorption bonds are weak, the inappropriate adsorption takes place, and the adsorption capacity decreases (31). If $n > 10$, the adsorption process is irreversible (32). The Freundlich isotherm constants can be obtained by drawing $\log(x/m)$ (or $\log q_e$) versus $\log C_e$ using the Eq 3 which is written in a linear form.

$$\text{Log} \left(\frac{x}{m} \right) = \text{Log} K_f + \frac{1}{n} \text{Log} C_e \quad \text{Eq (3)}$$

The slope and intercept of the obtained line are $1/n$ and K_f , respectively (30, 33). The Langmuir adsorption isotherm is the most important model for the one-layer adsorption (30). The Langmuir isotherm constants can be achieved by drawing $C_e/(x/m)$ versus C_e using the Eq 4 which is written in a linear form.

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad \text{Eq (4)}$$

Where K_L (L/mg) (or b) is the binding energy of the molecule adsorbed by the adsorbent's surface. The higher amounts of b show that the desorption hardly occurs for the adsorbed molecules, and these molecules are kept for a longer time on the surface. The Freundlich n illustrates the reaction between the adsorbent's adsorption sites and the adsorbed ions. If $n > 1$, the adsorption process is appropriate (34).

The Langmuir q_{\max} depicts the maximum adsorption on the adsorbent, and is one of the comparison criteria between the different adsorbents. The diagram of C_e/q_e versus C_e is linear in which the slope and intercept are $1/q_{\max}$ and $1/(q_{\max} K_L)$, respectively (31). The results are in agreement with two models, and have been presented in Table 1.

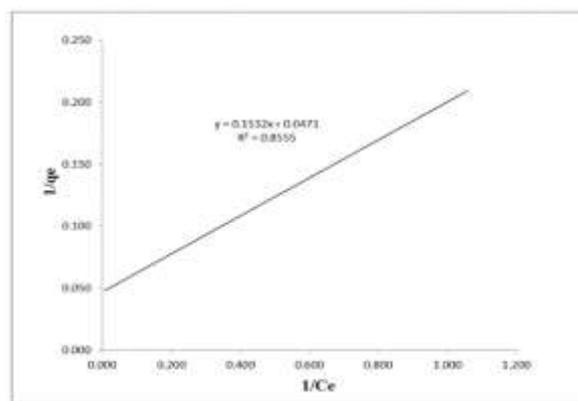


Fig 5: The Langmuir isotherm for the orange II adsorption using the tea waste (pH 2 and t 120 min)

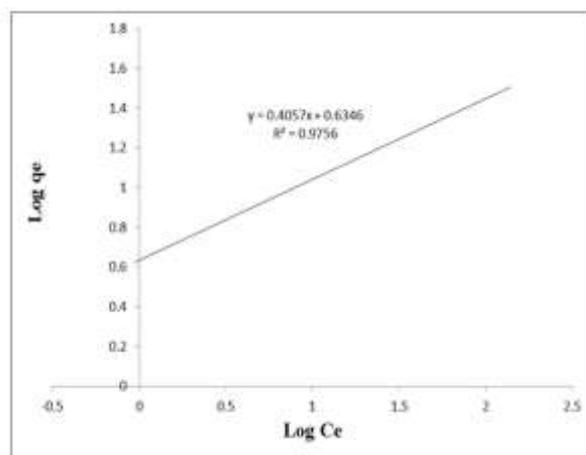


Fig 6: The Freundlich isotherm for the orange II adsorption using the tea waste (pH 2 and t 120 min)

Table 1: The Langmuir and Freundlich isotherm constants for the AO7 adsorption

Langmuir			Freundlich		
(mg/g)	K_L	R^2	$1/n$	K_f	R^2
q_{\max}	(L/mg)			(L/g)	
41.66	0.03	0.85	0.405	0.63	0.97

If $n > 2.47$, the adsorption process is suitable, and the amount of one-layer adsorption in the Langmuir model is about 42 mg/g. The amount of one-layer adsorption is used for comparing the adsorbents. The amount of adsorption in the canola waste (34), brewery waste (22), and unmodified biomass alga (11) is 24.57, 30.50, and 35.62, respectively.

However, in some nano adsorbents such as polypyrrole nanofibers (35), oyster shell supported zero valent nano scale iron (36), or the modified samples like palygorskite (15), higher amounts of adsorption were reported. The main properties of the tea waste in comparison with the synthetic and modified

adsorbents is that it is natural, and does not depend on the pH.

Conclusion

The results showed that the most orange II dye adsorption is 41.66 mg per each gram of fine-grained tea. The highest yield was obtained about 98% at pH 2 and t 120 min using 50 mg/L dye concentration and 10 g/L adsorbent. Also, the results indicated that this adsorbent has the slow adsorption process which causes that despite the other adsorbents, it does not depend on the pH so this property leads to the suitable removal yields.

The adsorption data is in agreement with two models but the correlation coefficient in the Freundlich model is more than the Langmuir model. The amount of n coefficient in the Freundlich model shows the appropriate physical adsorption of pollutants. According to the granulated structure of CTC tea waste (fine-grained tea) in three forms of raw, acidic, and calcined, it is a suitable and low-cost adsorbent in the orange 7 dye adsorption from the aqueous solutions.

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