

Original Article

Evaluation of Maize Tassel Powder Efficiency in Removal of Reactive Red 198 Dye from Synthetic Textile Wastewater

Mahboobeh Dehvari M.Sc., Mohammad Taghi Ghaneian Ph.D., Fatemeh Fallah B.Sc., Monireh Sahraee B.Sc., Behzad Jamshidi M.Sc.*

Department of Environmental Health, Shahid Sadoughi University of Medical Sciences, Yazd, Iran.

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Abstract

Introduction: Colored compounds which are often toxic and carcinogen is one of the environmental pollutants. These pollutants should be removed prior than discharge to the environment. The aim of this study was the evaluation of maize tassel powder efficiency for the removal of reactive red 198 dye from synthetic textile wastewater.

Materials & Methods: This experimental study was performed in laboratory scale by using of batch reactors. In this study, the effect of adsorbent dose, contact time, initial dye concentration and pH had been evaluated. Maximum adsorption wavelength (λ_{max}) and the concentration of dye were determined by UV/Vis spectrophotometer. The adsorbent was prepared in laboratory conditions and pulverized by standard ASTM sieves with the range of 40-60 mesh. The data were analyzed with Langmuir and Freundlich isotherm models.

Results: The result showed that the increase in adsorbent dose led to increasing of the adsorption efficiency. While, adsorption efficiency was decreased with elevation of pH from 3 to 9 and increasing of dye concentration from 25 to 50 mg/l. With the increase in reaction time, adsorption efficiency increased and the most adsorption occurred in the first 30 min of reaction. Our findings were in good concordance with both Langmuir and Freundlich isotherm models. The adsorption kinetics followed the pseudo-second-order equation.

Conclusion: Maize tassel powder is a natural and cheap adsorbent that can be used for the removal of contaminants in the environment.

Keyword: Inflorescence; Adsorption; Kinetics; Waste Water; Textiles, toxicity; Environmental Pollutants; Coloring Agents

* **Corresponding author:** *Tel:* +989171506432, *Email:* behzadjamshidi65@yahoo.com

Introduction

One of the largest water consuming industries is Textile industry. Depending on the type of production process, the amount of water used in this industry is between 25 to 250 cubic meters per ton of product ^[1]. Each year, nearly 10,000 different types of dyes and pigments are produced throughout the world ^[2]. The colors used in textile industry divided to Anionic (acidic, direct, reactive), cationic (all basic dyes) and nonionic (disperse dyes) groups ^[3]. Wastewater of textile industries commonly contains a variety of synthetic colors that have carcinogenic and mutagenic properties and are very stable in sunlight ^[4, 5, 6]. Colored wastewaters usually contain pollutants such as acids, alkalis, dissolved solids, toxic compounds and color ^[7]. The discharge of dye wastewaters from textile industries, not only affect on aesthetic aspects of receiving waters also caused the process of photosynthesis reduced. These wastewaters are considered as one of the most important environmental risk factors around the world ^[8, 9]. The Reactive dyes, which used in the dyeing process, are water-soluble and anionic ^[10, 11]. Their adsorption on the biological masses is weak and does not degrade under aerobic conditions^[6]. Reactive azo dyes are the largest group of water-soluble synthetic dyes and have the most variety in terms of type and structure ^[12]. Treatment of dyes is difficult and not effective with conventional wastewater treatment systems ^[13]. Treatment of textile wastewaters by physical, chemical and biological processes or combination of these

methods is possible ^[14]. Because of color stability against biological degradation, physical and chemical methods such as coagulation-flocculation, membrane processes, adsorption separately or combined with biological processes can be used ^[5,15]. Most of these methods have a high initial and operating cost ^[2]. One of the efficient methods for the removal of dye from textile wastewater is adsorption that in it used from the various adsorbents such as activated carbon, ash, rice husk and chitosan ^[15, 16, 17]. Activated carbon is the most widely used adsorbent for removal of some undegradable organic pollutants, but activated carbon is expensive ^[18, 19]. Therefore, researchers are looking for new and low-cost adsorbents and some researchers have been done for the development of low-cost adsorbents such as charcoal and kernel olive ^[20], biological solids ^[16], zeolite, agricultural wastes and biological adsorbents same as chitosan ^[21]. Tassel is corymbs' of maize plant that forms on top of the stem. The fiber parts of the plant are rich carbohydrates. Hydroxyl, carbonyl and amine groups on its surface can provide linked sites for the metal cations. Tassel is an agricultural waste that has shown good potential for the removal of heavy metals^[22]. Therefore, the aim of the current study was the evaluation of tassel powder as a natural adsorbent in removal of reactive red 198 dye from synthetic textile wastewater.

Materials & Methods

Chemicals and materials

Reactive red 198 dye (RR198) was obtained

from Dye Star Company. Other used materials were obtained from Merck Company.

Properties of the RR198 have been presented in Table 1 and Figure 1^[21, 23].

Table1. Properties of RR198 dye

Chemical formula	γ_{\max} (nm)	Molecular weight (g/mol)	Commercial name
$C_{27}H_{18}ClN_7Na_4O_{15}S_5$	518	967.5	Remazol Red 133

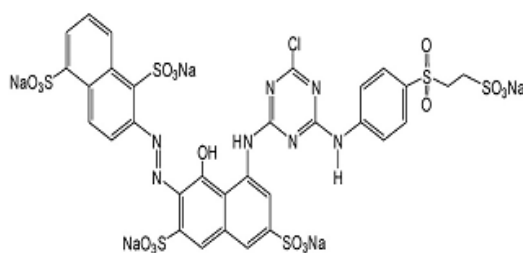


Figure1. Molecular structure of RR198 dye

Preparation of the tassel powder

Firstly Tassel were collected, milled and then in order to eliminate any impurities, washed with distilled water. To improve adsorption, adsorbents were boiled in distilled water for 10 minutes. At that time adsorbents dried at 102°C for 24 hours. Finally, adsorbent pulverized by standard ASTM sieves with the range of 40 to 60 meshes.

Analytical methods

The stock solution was prepared by dissolving a known amount of RR198 in 1L distilled water and was diluted to the required initial concentrations (25 and 50 mg/l). The pH of solutions was adjusted with NaOH and H₂SO₄ (0.1N) using pH meter Mi 151. The residual concentrations of dye in the samples were detected by UV-Visible spectrophotometer (Optima SP-3000 Plus model, Japan) at 518 nm.

In this study the variable factors were dye initial concentrations (25 and 50 mg/L), adsorbent dose (0.05, 0.075, 0.1, 0.125, 0.15 and 0.2 g/100 ml), contact time (15, 30, 60, 90, 120, 180, 240 minutes) and pH (3, 5, 7, 9).

The experiments were carried out by a mechanical shaker (INNOVA 40R, England) which its shaker speed was 120 rpm at 20°C. After shaking, samples were filtered by 0.45 μm filter paper and the filtrate was analyzed. The amount of dye adsorbed in mg/g at time t (q_e) and the percentage of removing dye (R) in solution were computed using formulae (1) and (2), respectively:

$$q_e = \frac{(C_0 - C_t)V}{M} \quad (1)$$

$$R (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

Where C_0 and C_t are the initial and at a given time dye concentrations (mg/L), respectively. V is the volume of the dye solutions (ml) and M is the weight of adsorbent (g) [19, 24].

Adsorption isotherm studies

Adsorption isotherms are basic requirements to design the adsorption systems [19, 25]. To determine isotherm models, different amounts of adsorbent (0.05-0.2 g/100 ml) were added to dye solutions with concentration of 25 mg/l. After 24 h, remaining dye concentrations were determined by spectrophotometric method. This stage was done with optimum pH.

In this study, the results also were evaluated by various adsorption isotherms including the Langmuir and Freundlich isotherms. The Langmuir model takes the following linear form:

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

Where q_m is the quantity of required adsorbate to form a single monolayer on unit mass of adsorbent (mg/g); q_e is the amount of adsorbed pollutant adsorbed on unit mass of the adsorbent (mg/g); C_e is the equilibrium concentration of solution (mg/L) and K_L (L/mg) is Langmuir constant that is related to the apparent energy of adsorption.

A plot of C_e/q_e versus C_e enables the determination of isotherm constants q_m and b from the slope and intercept, respectively [19, 21].

The essential characteristic of the Langmuir isotherm can be expressed by separation factor

or equilibrium parameter, R_L , which is defined by:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

Where C_0 is the initial dye concentration and K_L is the Langmuir constant. R_L values indicate the type of isotherm to be linear ($R_L=1$), irreversible ($R_L=0$), favorable ($0 < R_L < 1$) or unfavorable ($R_L > 1$) [21].

In Freundlich isotherm, the amount of solute adsorbed, (q_e), is related to the equilibrium concentration of solute in solution, (C_e), as follows:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (5)$$

Where n and K_F (L/mg) are isotherm constants which they indicate the intensity and capacity of the adsorption, respectively. Then and K_f constants were obtained from the plot of $\log q_e$ versus $\log C_e$ with a slope of $1/n$ and intercept of $\ln K_f$ [21]. The $1/n$ values indicate the type of isotherm to be irreversible ($1/n=0$), favorable ($0 < 1/n < 1$), unfavorable ($1/n > 1$) [26].

Adsorption kinetic studies

Adsorption kinetics study was carried out in order to test the relationship between contact time and dye uptake [4]. To determine of kinetic models, 0.2g of adsorbent material added to 100 ml of dye solution with concentration of 25 mg/l. The temperature and pH were kept constant throughout the experiment. Samples were withdrawn at different time intervals (2-120 min and 24 h). In this study, pseudo-first and pseudo-second-order adsorption models were investigated. A form of

pseudo-first-order model equation was described by Lagergren in the form:

$$\log(q_e - q_t) = \log q_e - \frac{K_f}{2.303} t \quad (6)$$

Where q_e and q_t (mg/g) refer to the amount of dye adsorbed at equilibrium and at time t , respectively. The k_f is the pseudo-first-order rate constant (min^{-1}).

The pseudo-second-order kinetics expressed in a linear form as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e t} \quad (7)$$

Where the q_e is equilibrium adsorption capacity and the k_2 (g/mg.h) second-order

constants can be determined from the slope and intercept of plot t/q_t versus t [24].

Results

Effect of pH

The results of the effect of pH on removal efficiency are shown in Figure 2. Based on the results, dye adsorption is highly pH dependent and with increasing pH, dye removal decreased, so that the removal efficiency (amount of adsorbed dye at equilibrium time) for initial dye concentration 25 mg/l were 97% in pH 3 and 24% in pH 9, while for initial dye concentration 50 mg/l were 46.8% and 1%, respectively.

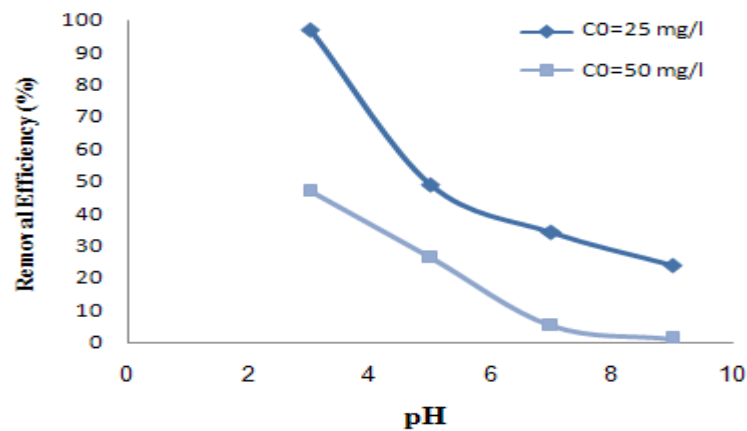


Figure 2. The effect of pH on removal efficiency of RR198 dye

Effect of adsorbent dose

The effect of adsorbent dose on the removal efficiency of reactive red 198 dyes is shown in Figure 3. Based on the data presented in Figure 3 with increasing of adsorbent dose from 0.05 to 0.2g /100ml, removal efficiency increased.

In adsorbent doses of 0.05 and 0.2 g/100 ml, the removal efficiency for initial concentration of 25 mg/ l were 62% and 95.62% and for initial concentration of 50 mg/ l were 40% and 84.1% , respectively. According to the results, the optimum adsorbent dose was 0.2 g /100 ml that was used for the other stages.

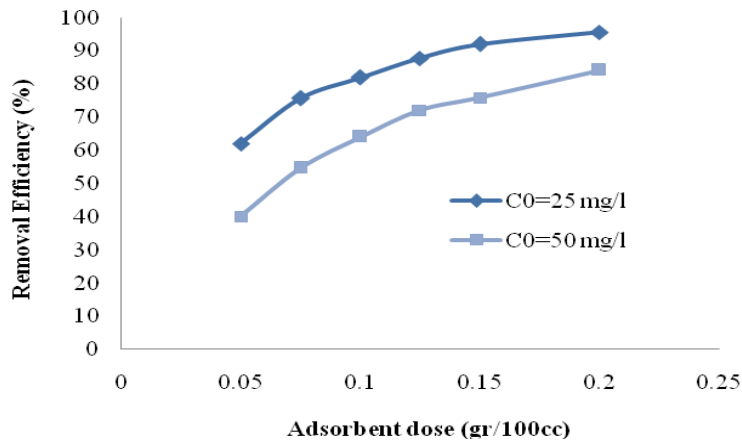


Figure 3. Effect of adsorbent dose on the removal efficiency of RR198 dye

Effect of contact time and initial dye concentration

The effect of contact time on the removal efficiency is presented in Figure 4. The results of this study showed that with increasing reaction time, efficiency of adsorption increased and maximum adsorption achieved in 30min. After this time, the increase has not considerable. The results show that removal

efficiency for concentrations of 25 and 50 mg, at 2 min were 46% and 41.4% and at 30 min were 89.76 and 78.28, respectively.

According to the results, removal efficiency decreased with increasing of dye initial concentration from 25 to 50 mg/l. The removal efficiency of dye for 120 min contact time and the initial concentrations of 25mg/l and 50mg/l were 90.48% and 81.88%, respectively.

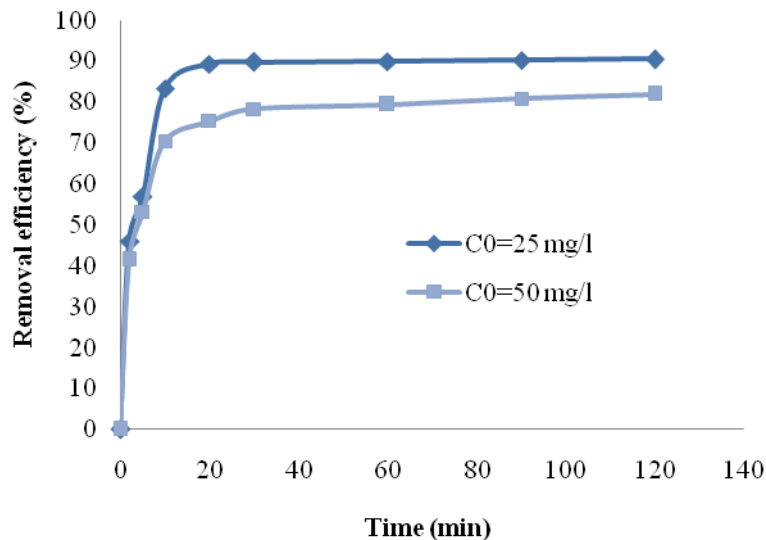


Figure 4. Effect of initial dye concentration and contact time on the removal of RR 198 dye
Adsorption isotherms

The achieved results from isotherm studies (Figures 5 and 6) showed that RR198 removal by tassel powder followed Langmuir and Freundlich isotherm models with high R^2 value. R^2 value in Langmuir and Freundlich isotherms for concentration of 25 mg/l was

equal to 0.944 and 0.989, respectively. Isotherm constants are presented in Table 2.

R_L and $1/n$ values (Table 2) are between zero and one that confirms the Langmuir and Freundlich isotherms are favorable for dye adsorption.

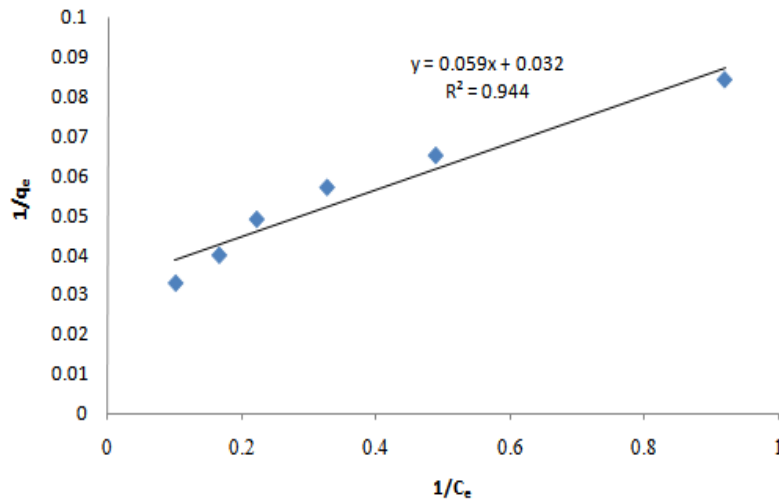


Figure 5. Langmuir isotherm model for RR198 adsorption on tassel powder (Initial dye concentration: 25 mg/l)

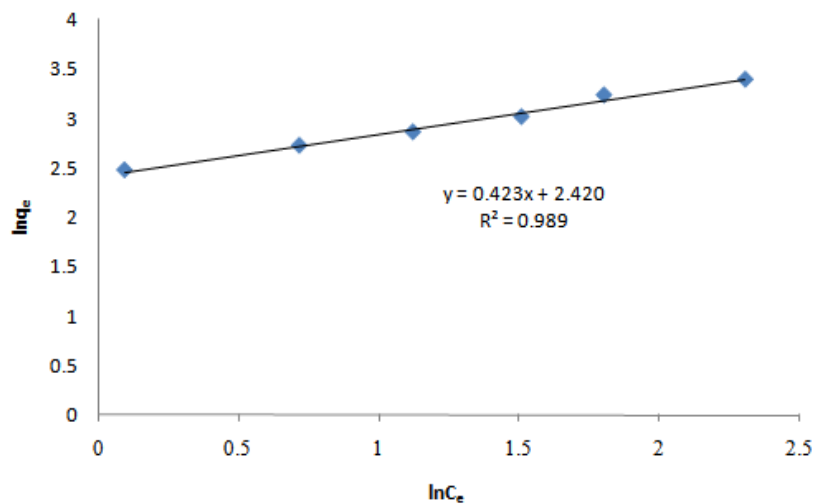


Figure 6. Freundlich isotherm model for RR198 adsorption on tassel powder (Initial dye concentration: 25 mg/l)

Table 2. Characteristics of adsorption isotherms (Initial dye concentration: 25 mg/l)

Langmuir isotherm		Freundlich isotherm
		K_f (mg/g).(L/mg) ^{1/n}
B(L/mg)	1.845	11.246
q_{max} (mg/g)	16.95	1/n
R_L	0.021	0.423
R^2	0.944	R^2
		0.989

Adsorption kinetics

Figure 7 shows results from the pseudo-first-order and pseudo-second-order kinetics. Relation constants of each model are calculated and presented in Table 3. The q_e theoretic value ($q_{e,cal}$) is lower than

experimental data ($q_{e,exp}$) which specifies that the adsorption process does not follow the pseudo-first-order reaction. We observed that adsorption of dye onto tassel powder fitted with pseudo-second order kinetic with the correlation coefficient (R^2) value 0.999.

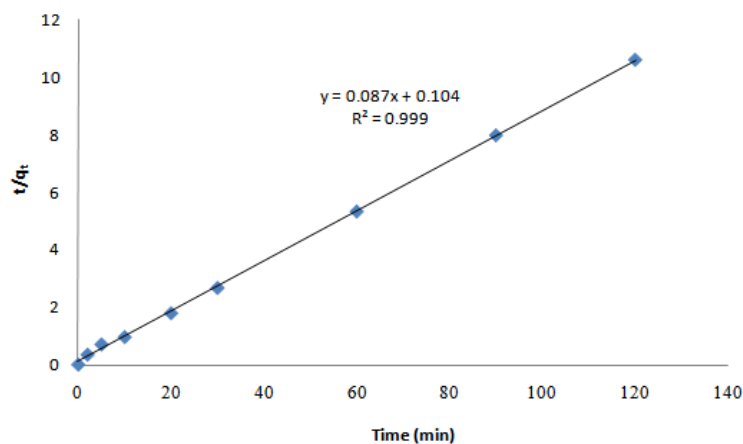


Figure 7. Pseudo-second-order kinetic for RR198 adsorption on tassel powder (Initial dye concentration: 25 mg/l)

Table 3. Characteristics of adsorption isotherms (Dye initial concentration: 25 mg/l)

First-second-order kinetic		Pseudo-second-order kinetic	
q_e (calc.)(mg/g)	3.343	q_e (mg/g)	11.494
q_e (exp.)(mg/g)	11.952	K_2 (g/mg.min)	0.073
K_1 (min ⁻¹)	1.207	R^2	0.999
R^2	0.498		

Discussion

The one of the important quality parameter in wastewater is pH. The pH value of the solution, affects on the surface charge of the adsorbent and the efficiency of the process [27]. According to the results of this study, with decreasing pH, removal efficiency is increased; so at pH=3, adsorption of reactive red 198 dye on the tassel is done with high efficiency. This might be occurred because of increasing of the H^+ ions in solution ($pH < pH_{zpc}$) and increasing of positives ions on adsorbent surface [28].

The results of Zvinowanda et al. study about heavy metal remediation by maize tassel showed that the adsorption capacity of the tassel on Cr (VI) decreased with increase in solution pH [29]. Ong et al. used for ethylenediamine modified rice hull as a new adsorbent for removal of blue basic dye and reactive orange 16. These researchers reported that with increasing of pH, removal efficiency of blue basic dye increased but removal efficiency of reactive orange dye16 decreased that this is because of changing in pollutant and charge of adsorbent surface in various pH [17].

Effect of adsorbent dose and determine the optimal mass of adsorbent used in adsorption processes is one of the most important issues that must be considered. According to our study results with increasing of adsorbent dose, dye removal efficiency increased. This phenomenon is associated with increasing of available surface area to adsorption of pollutants [21]. Zvinowanda et al. (2009) carried out adsorption studies of Cr (VI) and Cd (II)

using the maize tassel. In their study, the adsorption capacity of Cr (VI) decreased and adsorption of Cd (II) increased with increase in the adsorbent dose [29]. Mittal et al. (2010) considered the potential use of coconut husk (CH), for the removal of Quinoline Yellow dye from wastewater. Their results showed that adsorption increases with increase in the amount of adsorbent [30]. These results agree with those reported by Elkady et al (2011) and Ghaneian et al. (2012) [21, 27].

Changes in the initial concentration of pollutants are another factor that can effect on adsorption process. The results of this study showed that with increasing of initial concentration from 25 to 50 mg/l, removal efficiency decreased. With increasing of initial concentration, available activated sites for adsorption remained constant but the number of pollutants molecules in reactor increased [25]. Such results confirmed by ghaneian et al. (2011) and Ehrampoush et al. (2011) [31, 32]. According to results of Zvinowanda et al. (2009) study, the adsorption of Cr (VI) ions by maize tassel initially increased rapidly with increasing Cr (VI) concentration and slowed down when Cr (VI) concentration reached 300 mg/L but there was a general increase in adsorption of Cd (II) up to a concentration of 300 mg/L and then remained almost constant [29].

The results showed that to increase in contact time, removal efficiency increases. However the maximum adsorption is achieved in 30 minutes, then the amount of adsorption remains constant. In this time amount of

adsorbed dye with amount of desorbed are in equilibrium. In Ehrampoush et al. study about the use of eggshell as an absorbent in the removal of reactive red 123 dye found that with increasing of contact time, removal efficiency increased and maximum amount of adsorption in first 60 min of reaction achieved [32]. In Zvinowanda et al. study, there was a general increase in the percentage of adsorption of Cr (VI) and Cd (II) with time. The adsorption slowed down after about 120 min (Cr (VI)) and it then leveled off after about 200 min (Cd (II)) [29]. Olorundare et al. studied the potential application of activated carbon from maize tassel for the removal of heavy metals in water. They founded that by increasing the contact time, adsorption capacity increased [33]. Isaac et al. in their study about the comparison of modified and unmodified maize tassels for removal of selected trace metals in contaminated water found that this sorbent removed approximately 95% of the metals in less than 10 min [34]. The adsorption isotherms are equations for an explanation of adsorbate equilibrium state between solid phase and fluid. Values of correlation coefficient (R^2) are regarded as a measure of the goodness-of-fit of experimental data on the isotherm's model.

The results show that data fit with Langmuir and Freundlich models but R^2 value for the Freundlich isotherm was higher than 0.95 ($R^2=0.989$) which indicate a very good fit. According to table 2, amount of $1/n$ is less than 1 that describes Freundlich isotherm models and suggests that the process was controlled by

order chemisorption. In Ehrampoush et al. study of adsorption of reactive red dye 123 onto eggshell reported due to the upper amount of R^2 adsorption data accordance's with both Langmuir and Freundlich isotherm models and the reason of election of them explained by high R^2 [32]. Olorundare et al. also were achieved similar results. In their study, the adsorption process was described by both the Langmuir and Freundlich isotherms with R^2 values of 0.957 and 0.972, respectively [33].

In order to investigate the adsorption mechanisms, kinetic models were used to fit the experimental data. For most models for adsorption kinetics, are pseudo-first-order and pseudo-second-order models, for the removal of reactive red 198 dye on tassel, these models have been used. Kinetic studies revealed that the adsorption kinetics of reactive red 198 on powder tassel follows the pseudo-second order equation.

This equation is based on the assumption that the reaction rate determining step may be chemical sorption that valence forces through the sharing or exchange of electrons between adsorbent and the dye molecules may be involved. Zvinowanda et al. in their study founded that the kinetic of Pb (II) on tassel surface followed by pseudo-second-order (0.999) [35]. In an Amin study, on the removal of direct blue-106 dye using new activated carbons developed from pomegranate peel, he found that adsorption kinetics to follow pseudo-second-order rate kinetic model, with a good correlation ($R^2>0.99$) [19].

Similar results were also reported by Wang et al. (2010) [36].

Conclusion

In conclusion, results showed that maize

tassel powder is effective matter in dye removal. maize tassel powder is a natural and cheap adsorbent that can be used for the removal of contaminants in the environment.

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