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Full Length Research Paper

Novel herbal adsorbent based on wheat husk for reactive dye removal from aqueous solutions

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In the present study, wheat husk was applied as a natural adsorbent for the dye C. I. Reactive Yellow 15 removal from aqueous solutions. Different effective parameters of the decolorisation process such as contact time, stirring speed, temperature and pH of solutions were studied and the best condition for achieving the highest efficiency was introduced. It was found that the wheat husk activated with the solution of $HClO_4$ has a higher adsorption capacity. The optimum reaction time, at the speed of 50 rpm, is 70 min. At very acidic and natural pH and at the temperature of 30°C, C. I. Reactive Yellow 15 was removed more effectively. The Longmuir isotherm was found to be the most appropriate isotherm for describing the adsorption behavior of the reactive dye on wheat husk.

Key words: Adsorbent, wheat husk, reactive dye, decolorization, wastewater.

INTRODUCTION

Effluent or wastewater is a main pollutant of the environment. Over the past decades, increased attention has been directed to this issue, and many efforts have been made to clean up the environment. Different methods have also been developed for the treatment of effluent, most of which are too expensive.

Great importance has been attached to textile industry in terms of its environmental impact, because it consumes considerably high amounts of processed water and produces high quantities of polluted discharge colored wastewater including a great amount of dyes and chemical additions.

In textile industry, wastewater may be produced from various sources causing discharge of suspended particles (in different sizes, example, colloids), acidic or basic agents, heavy metals and soluble toxic compounds into the water (Correia et al., 1994; Banat et al., 1996; Uygur, 1997; O' Neill et al., 1999; Vandevivere et al., 1998). For example, each of the washing (scouring), bleaching, mercerization, dyeing, printing and finishing processes can produce different types of wastewaters.

The resulted effluent leading to the formation of the mentioned processes usually have a high temperature and pH and contains a large volume of organic non-biodegradable chemicals such as soaps, detergents, waxes, (in washing process), chlorine and peroxide compounds (in bleaching process), heavy metals caused by dyeing reactions, starches and various toxic chemicals that are usually used in finishing processes. Great amounts of salt in dye bathes (typically up to 100 g/l) make the treatment and discharge of the wastewater more complicated. Hence, textile effluent treatment procedures usually encounter two main problems: firstly, the decolorisation and secondly the salt purification of the effluent. Furthermore, most of the dyestuffs are water soluble and not degradable under non-aerobic biologic treatment conditions (Uygur and Kök, 1999; Tüfekci et al., 2007; Leonas and Michael, 1994; Manu, 1999).

Discharge of the pollutant wastewater into the environment is undesirable; therefore, the effluent from textile processes has to be treated before it is released. Conventional treatment methods can mainly be divided into the physical, chemical and biological subgroups. In spite of a relatively good efficiency, these methods usually encounter difficulties when high amounts of tint and color of the wastewater exist, which is actually one of the main problems in treatment processes. In this way,

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Table 1. Basic components in wheat husk.

Component (%)	Percentage
Cellulose	36
Hemi cellulose	18
Lignin	16
Starch	9
Protein	6
Fat	5

complementary methods must be applied to treat the effluent (Jeric et al., 2009; Ahmad et al., 2002). Complementary methods such as floating, coagulating and oxidation have problems that reduce their effectiveness in terms of lowering the color of effluent. For instance, coagulating method cannot eliminate the dye molecules. Using adsorbent materials is an economical and optimized method. These materials can be divided into two groups: 1) mineral adsorbents, example, active carbon, caulen, bentonit, talk and (2) herbal adsorbents such as wheat and rice husk.

After the extraction of wheat grain, wheat husk is generated in large quantities. Wheat husk is considered to be a kind of waste material. In order to get rid of this huge amount of wheat husk, farmers use only a small volume of it in agricultural farms as a fertilizer and usually burn the rest of it in open air, and this might cause environmental problems. Therefore, it is necessary to properly manage and use the burnt residues in order to reduce their environmental impact including land and air pollution (Bledzki et al., 2010; Zhang and Mkhatib, 2008; Ganesan et al., 2007; Serkan et al., 2008).

Wheat and rice husks can be used in making concrete for partial replacement of cement (Bledzki et al., 2010). Presence of husks improves some properties of the concrete such as compressive strength (Ganesan et al., 2007). Some basic chemical properties of wheat husk are given in Table 1 (Serkan et al., 2008). The mechanism of dye adsorption by adsorbent materials can be explained using three steps (Manu, 1999):

1. The adsorbent attacks the dye bonds and causes their reduction through breaking the molecules.
2. The adsorbent reduces the simple oxochrome groups via breaking them.
3. The adsorbent may reduce the dye molecule by changing its resonance.

The purpose of this work was to investigate the capability of wheat husk as a bio-sorbent for removing anionic dyes from the aqueous solution, and a rapid inexpensive system for the removal of dyes from textile industry has been developed.

MATERIALS AND METHODS

Preparation of wheat husk

All chemicals and reagents used in this work were of analytical purity grade. The wheat husk was from Mazandran farm in the north of Iran and was extensively washed with water in order to remove soil and dust, and it was air dried. The wheat husk was dried in an oven at 65°C for a period of 3 h. Finally, it was ground and sieved (meshes 2 to 35). The chemical modification of wheat husk was made according to the similar method previously described by Vaughan et al. (2001). The wheat husk adsorbent was activated by stirring in 1 mol/lit solutions of HNO_3, HCl, H_2SO_4, $HClO_4$, H_3PO_4 and NaCl. Then, the activated adsorbent was washed with distilled water and filtered using a suction device. At the next step, the activated wheat husk adsorbent was added to a 200 cc solution of the reactive dye. Nitric acid and sodium hydroxide were used to control the pH of the solution.

Preparation of dye solutions

A reactive Yellow dye (C.I. Reactive Yellow 15), whose chemical structure is illustrated in Figure 1, was used in this study. All chemicals were supplied by Merck Chemical Corp. The pH of the solution was measured using ELICO, India LI 120 pH meter, and the concentration of Reactive dye was determined by a UV-Visible CINTRA 10 spectrophotometer. The stock solution had a concentration of 1 g/L of the dye. The percentage of dye removal after the treatment process was calculated by Equation 1:

$$R(\%) = (1 - \frac{c}{c_0}) \times 100 \quad (1)$$

Where, C_0 is the concentration of dye before decolorisation; C is the concentration after decolorisation and R is the dye removal percent.

RESULTS AND DISCUSSION

Effect of the activators

In order to investigate the effect of chemical modification on the C.I. Reactive Yellow 15 dye sorption of wheat husk, the removal capacities of modified wheat husk adsorbing C.I. Reactive Yellow 15 from aqueous solution were compared. The concentration of the activator and the experiment time were 1 mol/l and 1 h respectively. The obtained results are shown in Table 2, since the treatment of wheat husk with $HClO_4$ as an activator is very effective and can remove about 94.58% of C.I. Reactive Yellow 15 dye from aqueous solutions.

Effect of contact time (dye and adsorbent)

The effect of contact time between adsorbent and dye was evaluated and the concentration of dye and the volume of the solution were 100 mg/L and 200 cc, respectively. To evaluate the effect of contact time, the

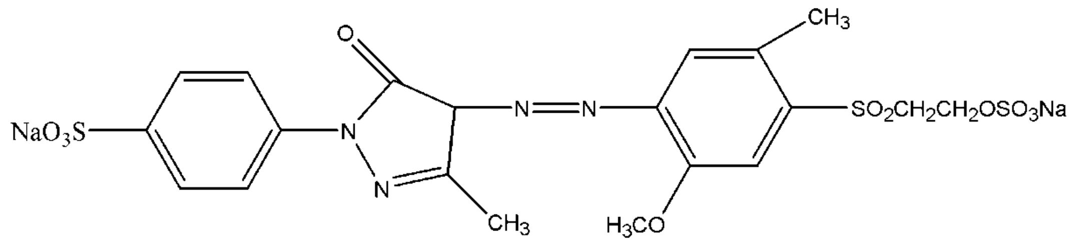

Figure 1. Chemical structure of the C.I. Reactive Yellow 15.

Table 2. The effect of different activators on wheat husk for decolorisation of C.I. Reactive Yellow 15 (room temperature).

Activator	$HClO_4$	HNO_3	HCl	H_2SO_4	H_3PO_4	NaCl	—
R%	94.58	88.15	87.55	86.69	85.08	59.14	46.77

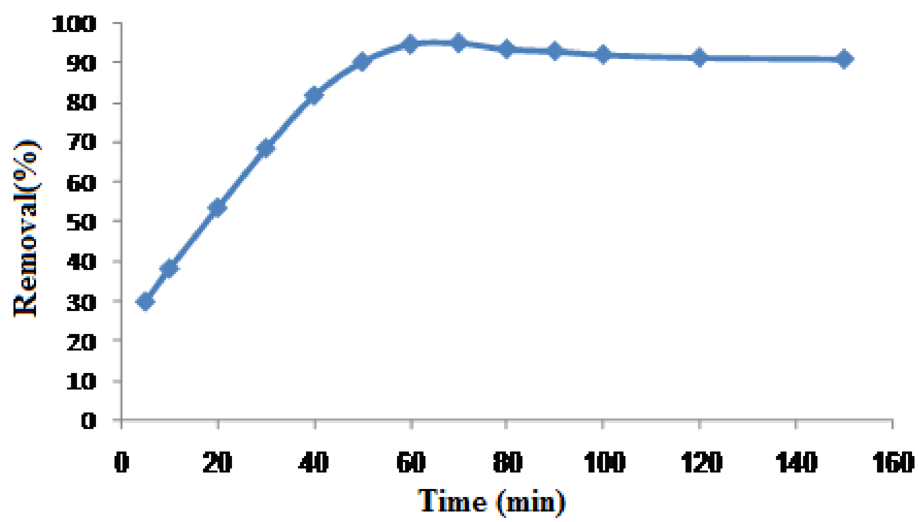

Figure 2. The effect of contact time on the adsorption of C.I. Reactive Yellow 15 using activated wheat husk.

stirring time at constant rpm (130) was varied between 0 and 160 min. The results are illustrated in Figure 2. As it is shown, the amount of dye removal increases up to 70 min and then slightly decreases until it reaches to a saturated state. In further studies, the stirring time of 70 min was selected to guarantee the equilibration state.

Effect of stirring speed

The effect of stirring speed was studied by changing the stirring speed of the instrument in the range of 50 to 300 rpm at a constant concentration and the stirring time of 70 min. The maximum amount of adsorption was observed at rpm of the 50, while at higher rpm, the dye molecules did not have enough contact time with the active sites of the adsorbent.

Effect of pH

The effect of sample pH on the sorption process was investigated. Decolorisation process was investigated at room temperature and in the pH range of 2 to 12. The results obtained in Figure 3 showed that the adsorption of dye is highly dependent on the pH of solution as well as the surface charge of the sorbent. As illustrated in this figure, in acidic (pH = 3) and neutral state, the highest amount of adsorption was achieved, while toward basic conditions, it decreased.

In acidic media (low pH), the active site on the sorbent is positively charged and can adsorb the reagent dye as a result of electrostatic attraction between negatively charged dye anions and positively charged adsorption sites and an increase in dye adsorption. Maximum removal of C.I. Reactive Yellow 15 with wheat husk was

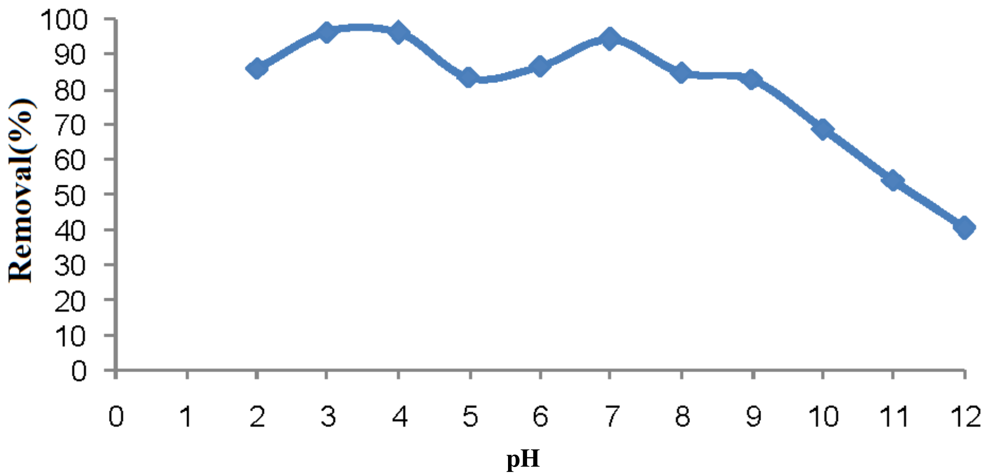

Figure 3. The effect of pH on the adsorption of C.I. Reactive Yellow 15 using activated wheat husk.

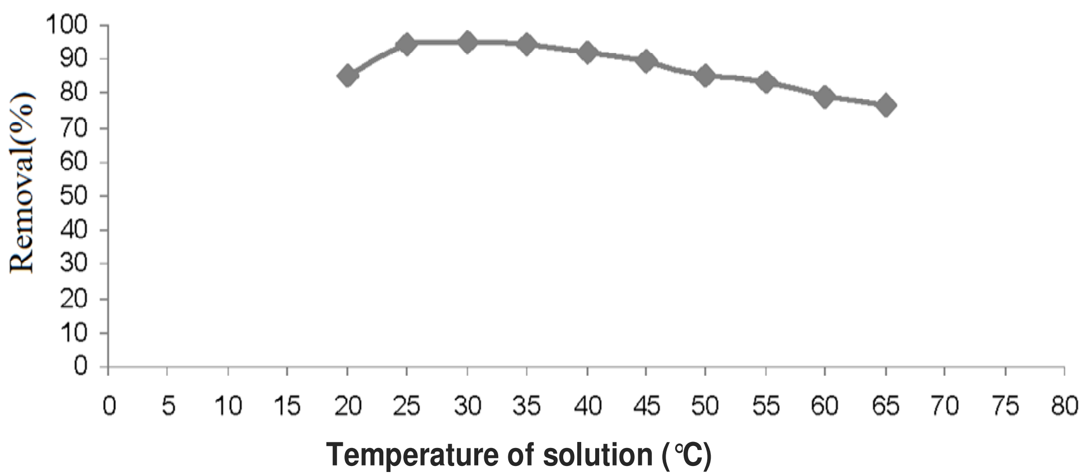

Figure 4. The effect of temperature on adsorption of C.I. Reactive Yellow 15 (pH 7 and contact time 70 min).

at acidic pH of 3. In basic media, the surfaces are probably negatively charged. It may be due to the abundance of -OH ions on sorbent which cause repulsion between the negatively charged surface and the anionic dye molecules. Besides, there are no exchangeable anions on the outer surface of the adsorbent at higher pH values, and consequently the adsorption decreases.

Effect of temperature

The decolorisation process was investigated at 10 different temperatures (20, 25, 30, 35, 40, 45, 50, 55, 60, and 65°C) when the solution was neutral (pH 7) and the concentration of dye was 0.1 g/L. As it is shown in Figure 4, the dye removal percent reaches a maximum amount at 30°C and then decreases. The dye removal for 65°C is the lowest. This is due to desorption of C.I. Reactive Yellow 15 from sorbent to the solution at high temperature. Nevertheless, as the uptake of C.I. Reactive Yellow 15 by wheat husk was fast and at room temperature, another experiment was conducted at ambient temperature.

Adsorption isotherm

The feasibility of adsorption on adsorbent for the removal of dyes can be demonstrated by adsorption isotherms. In order to determine the type of adsorption isotherm of the Reactive Yellow dye on the wheat husk, the temperature of 25°C (room temperature) was selected, and the data

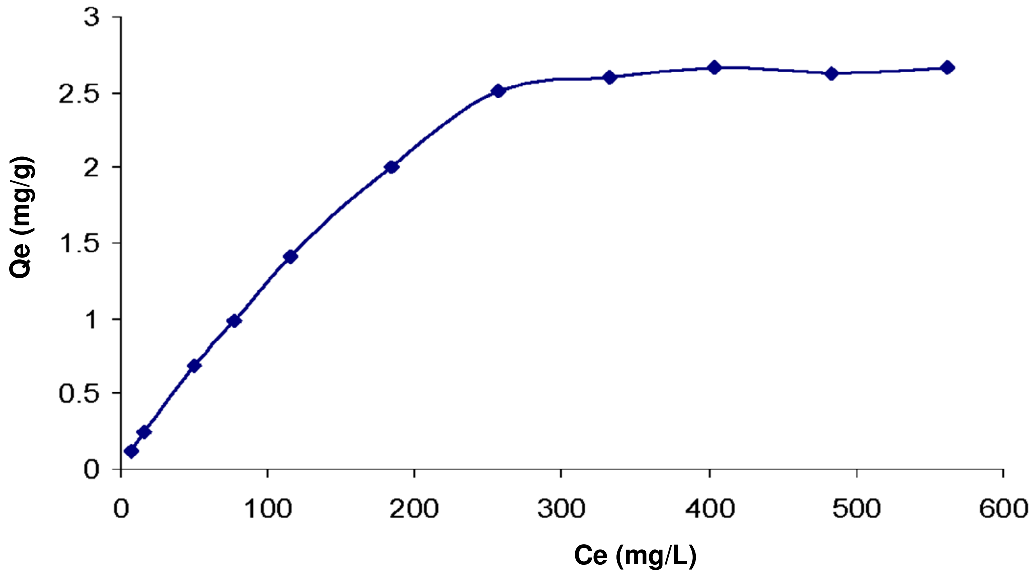

Figure 5. Adsorption isotherm for the dye C.I. Reactive Yellow 15 using activated wheat husk at 25°C.

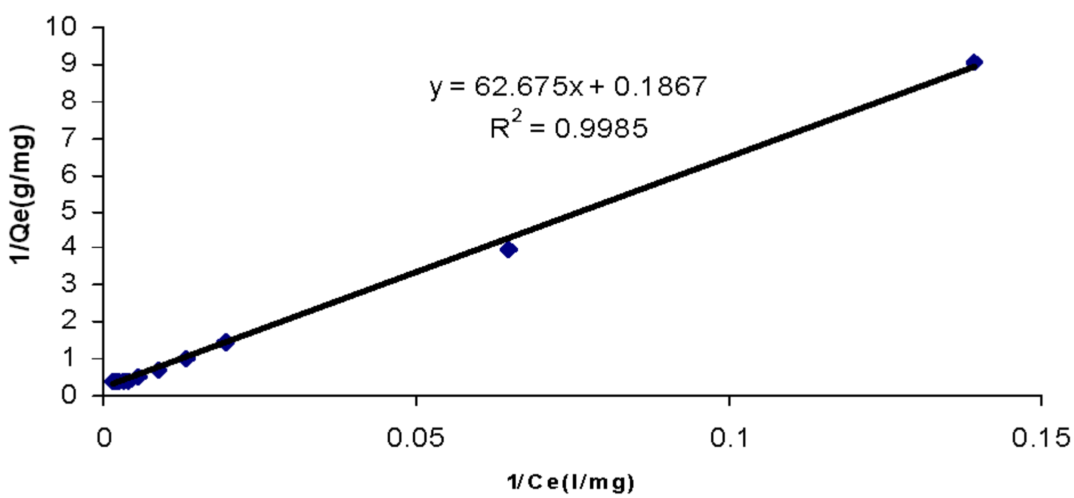

Figure 6. Langmuir isotherm for the dye C.I. Reactive Yellow 15 on activated wheat husk at 25˚C.

obtained for the dye removal at equilibrium by activated wheat husk was fitted into Langmuir and Freundlich adsorption models (Figures 5 to 7). The Langmuir adsorption isotherm is presented by Equation 2.

$$Q_e = \frac{K_1 \times Q_M \times C_e}{1 + K_1 \times C_e} \qquad (2)$$

Where, Q_e and C_e are dye concentration at equilibrium condition on the adsorbent (mg.g^{-1}) and in the solution (mg.dm^{-3}), respectively. Q_m is the adsorption capacity of the adsorbent (mg.g^{-1}) and K_1 (dm^3.mg^{-1}) is called the Langmuir adsorption constant. The Freandlich adsorption equation is as follows:

$$Q_e = K_f C_e^{\frac{1}{n}} \qquad (3)$$

Where, K_f and n are the Freandlich isotherm constants.

According to the obtained correlation values in Table 3, the best adsorption isotherm model for single layer adsorption of the reactive yellow 15 dye on the wheat husk is Longmuir isotherm. Hence, it can be concluded that there are sites on the wheat husk that either

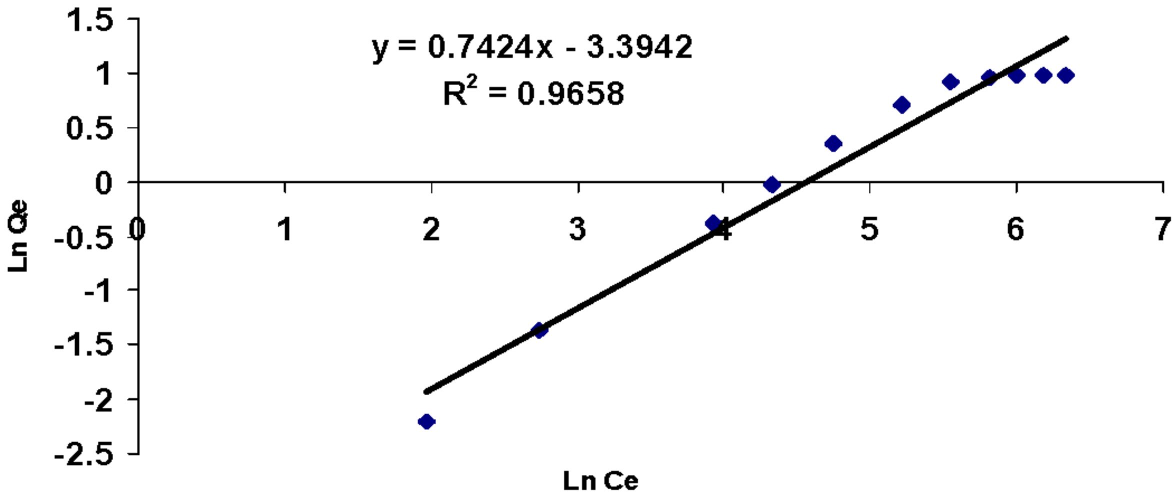

Figure 7. Freandlich isotherm for the dye C.I. Reactive Yellow 15 with activated wheat husk at 25°C.

Table 3. Isotherm parameter for the adsorption of reactive yellow 15 onto activated wheat husk at 25°C.

Model	Parameter value		R^2
Langmuir	K_l (L/mg) 0.002978	Q_m (mg/g) 5.3561	0.9985
Freandlich	K_f (mg/g)(L/g)^n 0.03356	n 1.3469	0.9658

chemically or physically adsorb the dye. By completely occupying the sites, saturation state in adsorption is achieved, which is actually the adsorption capacity of the Longmuir isotherm.

Conclusion

The present study showed that the wheat husk can be used as an adsorbent for the removal of C.I. Reactive Yellow 15 from aqueous solutions. Wheat husk is easily available in large quantities and the treatment method of bio-sorbent seems to be economical. Different effective parameters in the decolorisation process of dye solution were studied. The amount of dye sorbet was found to vary with initial solution pH, contact time, stirring speed and treatment of the wheat husk.

The decolorisation efficiency for the used reactive dye in very acidic and neutral conditions was higher. In addition, the temperature of 30°C, contact time of 70 min and stirring speed of 50 rpm were found to be conditions for achieving the best results. Longmuir isotherm was also found to be the best model for the adsorption behavior of the reactive dye on the wheat husk.

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