The removal of reactive dyestuff from aqueous solutions using activated carbon prepared from orange (*Citrus sinensis* L.) pulp by chemical activation with $ZnCl_2$

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Abstract

In this study, activated carbon was produced from orange (*Citrus sinensis* L.) pulp by chemical activation with zinc chloride ($ZnCl_2$) and an adsorption capacity of activated carbon for removal of reactive dyestuff (Blue 49) from aqueous solutions was investigated. The surface area of chemically modified activated carbon were 1779.48 m^2g^{-1}. The results indicated that the adsorption of Blue 49 obeys the pseudo-second-order model. The thermodynamic parameters such as ΔG°, ΔH° and ΔS° were calculated to estimate the nature of adsorption and these parameters indicate a feasible, spontaneous and endothermic adsorption. The results suggest that the activated carbon prepared from orange pulp has potential in remediation of reactive dyestuff (Blue 49) contaminated waters.

Keywords: Activated carbon, orange pulp, adsorption, characterization, Blue 49.

1. Introduction

Use of different types of dyes in industries producing textile, paper, rubber, plastic, leather, cosmetics, pharmaceutical and food stuff, is well known. The wide use of these dyes lead to a variety of environmental problems, especially water pollution (Yang and Qui, 2010; Mittal *et al*., 2009). Dyes may also be problematic if broken down anaerobically in the sediment, leading to the production of toxic amines. Some dyes have been reported to cause allergy, irritation, cancer and even mutation in humans (Deng *et al*., 2009; Angın *et al*., 2013). Among various treatment technologies, adsorption onto activated carbon has proven to be one of the most effective and reliable physicochemical treatment methods. However, commercially available activated carbons are usually derived from wood or coal, and therefore, are considered expensive (Wang *et al*., 2010; Angın, 2014). There is a need to produce low cost and effective activated carbons that can be applied to water pollution control. Therefore, many researchers have investigated cheaper and more efficient activated carbon production from industrial and agricultural wastes (Yang and Qui, 2010; Lin *et al*., 2013; Senthil Kumar *et al*., 2010; Angın, 2014; Sulak *et al*., 2007). The agricultural and food industries' wastes are considered to be very important precursor materials for activated carbon production since they are cheap, renewable, safe and available at large quantities from easily accessible sources. These wastes are usually disposed of by burning or by deposition in landfills, but conversion to higher-value products such as activated carbon would be preferable (Chen and Chen, 2009). Orange (*Citrus sinensis* L.) peels/pulp are one of these valuable waste materials discarded from juice industry. Therefore, this study has investigated the potential use of high surface area activated carbon prepared from orange pulp by chemical activation for the removal of reactive dyestuff (Blue 49) from wastewater.

2. Materials and Methods

2.1. Material

Orange (*Citrus sinensis* L.) pulp was supplied by the LIMKON Fruit Juice Factory, (Adana-TURKEY), and they were crushed and the fraction of particle sizes between 1 and 2 mm was chosen for subsequent studies. The reactive Blue 49 dye (C.I.621526) was obtained from SARAR Textile Factory (Eskisehir, Turkey).

a. Preparation and characterization of activated carbon

In this study, chemical activation of orange pulp was performed using zinc chloride ($ZnCl_2$). The orange pulp was mixed with $ZnCl_2$, in a ratio $ZnCl_2$:orange pulp mass ratio of 3:1. About 10 g of the impregnated sample was placed on a ceramic crucible in the tubular reactor (Protherm PTF 12) and heated up to the final activation temperature (500 °C) under the nitrogen flow (≈200 cm^3min^{-1}) at heating rate of 5 °Cmin^{-1} and held for 2 h at this final temperature. Proximate analyses of orange pulp and activated carbon were determined according to the international standards. The contents of carbon, hydrogen, nitrogen and sulpur of the orange pulp and activated carbon were measured using a LECO CHNS 932 Elemental Analyzer. The oxygen contents were calculated by difference. The BET (Brunauer–Emmett–Teller) surface area of activated carbon was determined from

nitrogen adsorption-desorption data by using Micromeritics Instruments, Tristar II 3020.

b. Adsorption experiments

The studied variables were initial pH, adsorbent dosage, contact time and temperature of solution. In the procedure for the batch pH studies, 0.4 g adsorbent and 100 mL of Blue 49 solution containing 100 mgL^{-1} Blue 49 were mixed and shaken at 298 K for 24 h using a temperature controlled water bath with a shaker (GFL). After adsorption, samples were filtered and then the concentration of Blue 49 in the supernatant solution was analyzed. All concentrations were measured by using UV spectrophotometer (Shimadzu UV-Vis 1240) at 204 nm. The initial pH values of the solutions were adjusted to different values (between 1 and 12) by adding dilute NaOH or HCl solutions. The pH was measured with pH-meter (Mettler-Toledo). After adsorption, the pH value providing the maximum Blue 49 removal was determined. Also, for the purpose of researched the effect of adsorbent dosage, batch experiments were carried out at 298 K and optimum pH value of the solution for 24 h shaking period by adding different amounts of activated carbon (0.05-0.8 g) into each 100 ml Blue 49 solution (100 mgL^{-1}). The removal percentage of Blue 49 was calculated according to the following equation:

$$Removal\ (\%) = \frac{C_0 - C_e}{C_o} x100 \quad (1)$$

Where C_0 and C_e (mgL^{-1}) are initial and equilibrium concentrations of the dyestuff (Blue 49), respectively (Yang and Qui, 2010).

Blue 49 uptake at equilibrium, q_e (mgg^{-1}), was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (2)$$

Where V (L) is the volume of the aqueous Blue 49, and w (g) is the weight of adsorbent (activated carbon).

Adsorption kinetic experiments were conducted by contacting 0.4 g adsorbent with 100 mL Blue 49 solution (100 mgL^{-1}) at 298, 308, 318 K and optimum pH (2.0) for 24 h with continuous shaking. The concentration of dyestuff in supernatant was determined at different time intervals.

In order to analyze the kinetic mechanism of adsorption process, the experimental data were fitted in the pseudo-first-order, pseudo-second-order, and intra-particle diffusion models which are described as Eqs. (3), (4) and (5);

Pseudo-first-order equation:

$$\log(q_e - \mathrm{q_t}) = \log q_e - \frac{\mathrm{k_1 t}}{2.303} \quad (3)$$

Pseudo-second-order equation:

$$\frac{\mathrm{t}}{\mathrm{q_t}} = \frac{1}{\mathrm{k_2 q_e}} + \frac{t}{q_e} \quad (4)$$

Intra-particle diffusion equation:

$$\mathrm{q_t} = \mathrm{k_p} t^{\frac{1}{2}} + C \quad (5)$$

Where q_t and q_e (mg g^{-1}) are amounts of Blue 49 adsorbed over a given period of time t and at equilibrium, respectively; t is the adsorption time (min); k_1 (min^{-1}), k_2 (g $mg^{-1}min^{-1}$), and k_p (mg $g^{-1}min^{-1/2}$) are the adsorption rate constant of the pseudo-first-order adsorption, the pseudo-second-order adsorption and the intra-particle diffusion, respectively; and C (mg g^{-1}) is a constant in the intra-particle diffusion equation, corresponding to the thickness of boundary layer (Huang *et al*., 2014; Angın *et al*., 2013; Demiral and Güzdüzoğlu, 2010). Three thermodynamic parameters, i.e. change in the Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$), were calculated to evaluate the thermodynamic feasibility and the nature of the adsorption process. $\Delta G°$ can be calculated according to the following equation:

$$\Delta G^o = -RT ln\ K \quad (6)$$

Where R is the gas constant (8.314 J $mol^{-1}K^{-1}$), T is the temperature (K), and K is the thermodynamic equilibrium constant of the adsorption process, reflecting dyestuff distribution between the solid and liquid phases at equilibrium. Equilibrium constant (K) was estimated as:

$$K = \frac{q_e}{C_e} \quad (7)$$

According to the van't Hoff equation:

$$\ln K = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (8)$$

The values of $\Delta H°$ (kJ mol^{-1}) and $\Delta S°$ (J $mol^{-1}K^{-1}$) were evaluated from the slope and intercept of van't Hoff plots (Huang *et al*., 2014; Lin *et al*., 2013).

3. Results and discussion

3.1. Characterization of activated carbon

The results of proximate and ultimate analyses and surface properties of the orange pulp and activated carbon are given in Table 1. As suggested by the study, the carbon content increased after activation process, and the hydrogen, nitrogen and oxygen content indicated the opposite change trend. Since the sulfur content of activated carbon was below the detection limit, the activated carbon could be used in adsorption and purification process. Also, activation process led to an increase in fixed carbon content while decrease in volatile matter content. The ash content of activated carbon was decreased by activation process. The porosity has a strong effect on the adsorption properties of the activated carbon. The specific surface area of activated carbon was found to be 1779.48 m^2 g^{-1} and the most of the material (≈78%) consist of micropores.

Table 1. Characteristics of the orange pulp and activated carbon.

Characteristics (wt%)	Orange pulp	Activated carbon
Moisture content	3.70	8.37
Proximate analysis		
Volatile Matter	82.70	9.18
Ash	2.80	0.57
Fixed carbon (by difference)	14.50	90.25
Ultimate analysis		
Carbon	45.05	56.57
Hydrogen	6.29	2.68
Nitrogen	1.66	2.77
Sulfur	0.03	0.08
Oxygen (by difference)	53.03	22.46
BET surface area (m^2 g^{-1})	0.704	1779.48

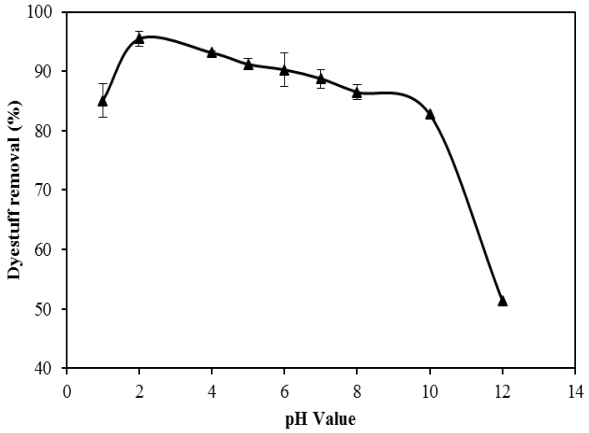

Figure 1. Effect of pH for the removal of Blue 49 onto activated carbon.

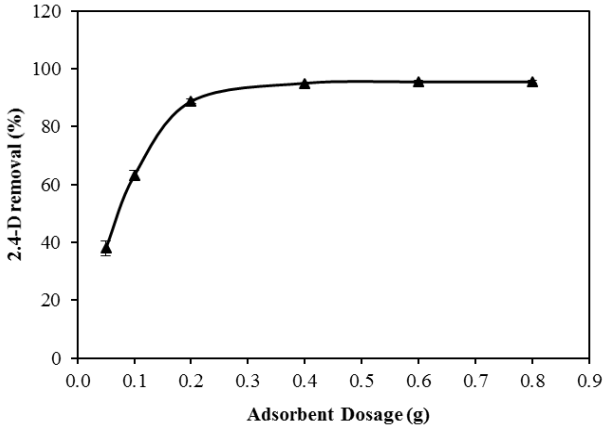

Figure 2. Effect of adsorbent dosage for the removal of Blue 49 onto activated carbon.

3.2. Effect of initial pH

In general, initial pH value may enhance or depress the dyes uptake, inter-correlated to the changes of adsorbent surface properties and dye chemistry (Foo and Hameed, 2012; Benadjemia *et al*., 2011). The effect of initial pH on the removal of Blue 49 was investigated in the pH range of 1.0-12.0 for activated carbon (Fig. 1). As shown in Fig. 1, removal of Blue 49 decreased from 95.45% to 51.33 because of the increase of pH from 2.0 to 12.0. Thus pH 2.0 was selected as the optimum pH value for all further experiments.

3.3. Effect of adsorbent dosage

The effect of dosage of activated carbon on the percentage removal of Blue 49 is shown in Fig. 2. It is apparent that the percentage removal of Blue 49 was increased by increasing the activated carbon dosage. This was the reason that the number of available adsorption sites was increased by increasing the adsorbent dosage (Wang *et al*., 2010). When the activated carbon dosage was 0.4 g/100 mL, the removal percentage of Blue 49 can reach 95.04%. The results also indicate that the removal efficiency increases up to the optimum dosage (0.4 g/100 mL) beyond which the removal efficiency is negligible.

3.4. Adsorption kinetics

Adsorption kinetic describes the controlling mechanism of adsorption processes which in turn governs the mass transfer and equilibrium time (Mestre *et al*., 2011). The experimental data of Blue 49 adsorption onto activated carbon at different time intervals were examined using pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models at different solution temperature. The pseudo-second-order kinetic plots for the adsorption of Blue 49 onto activated carbon at different solution temperature are given in Fig. 3. All the constants and the linear regression coefficient values of the models are given in Table 2. Based on the regression coefficients, the pseudo-second-order model appeared to be more suitable

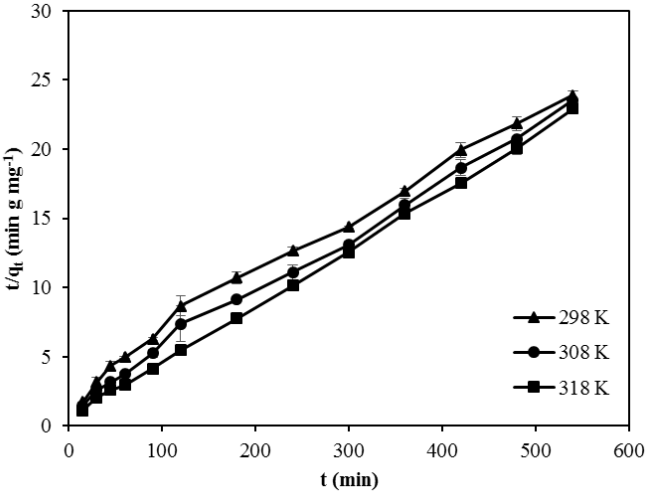

Figure 3. The pseudo-second-order kinetic plots for the adsorption of Blue 49 onto activated carbon.

Table 2. Kinetic parameters for the adsorption of Blue 49 onto activated carbon at different solution temperatures.

Solution Temperature (K)	298	308	318
$q_{e,exp}$ (mg g^{-1})	23.47±0.114	23.65±0.095	23.84±0.046
Pseudo-first-order			
k_1 (min^{-1})	0.0053	0.0062	0.0082
$q_{e,calc}$ (mg g^{-1})	15.97	15.47	14.95
R^2	0.9818	0.9628	0.9028
Pseudo-second-order			
k_2 (g $mg^{-1}min^{-1}$)	0.0164	0.0282	0.0751
$q_{e,calc}$ (mg g^{-1})	24.57	24.63	24.51
R^2	0.9918	0.9969	0.9994
Intra-particle diffusion			
k_p (mg $g^{-1}min^{-1/2}$)	0.7612	0.6577	0.4675
C(mg g^{-1})	6.099	9.710	14.904
R^2	0.9701	0.9049	0.8996

to describe the adsorption kinetic data. In addition, the calculated q_e values also agree with the experimental data in the case of pseudo-second-order kinetic model. Therefore the adsorption kinetic could well be approximated more favorably by pseudo-second-order kinetic model for Blue 49 adsorption. Similar results were also reported by other researchers (Angın *et al*., 2013; Xin-Hui *et al*., 2013; Demiral and Gündüzoğlu, 2010; Senthil Kumar *et al*., 2010).*3.5. Thermodynamic parameters.* Adsorption thermodynamics such as Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$) provide an insight into the mechanism and adsorption behavior of an isolated system. Its original concept assumes that energy cannot be gained or lost, which entropy change is the driving force (Lin *et al*., 2013). Positive value of $\Delta H°$ indicates endothermic. nature of adsorption process. Typically, $\Delta H°$ value for physical adsorption ranges from 4 to 40 kJmol^{-1}, compared to chemical adsorption which varies from 40 to 800 kJmol^{-1} (Foo and Hameed, 2012). In this study, the calculated $\Delta H°$ value was 11.46±2.38 kJmol^{-1}, indicating the reinforcement of physical adsorption process. The negative value of $\Delta G°$ (–3.33±0.24, –3.78±0.19 and –4.32±0.11 kJmol^{-1}) indicate the spontaneous nature of the adsorption for Blue 49 at 298, 308 and 318 K. Meanwhile, the value of $\Delta S°$ was 49.56±7.55 Jmol^{-1}K^{-1}, which indicated increased randomness at the solid-solution interface with the loading of Blue 49 molecules onto the external and internal surfaces of the carbonaceous substance.

4. Conclusion

In this study, orange (*Citrus sinensis* L.) pulp was converted into activated carbon by chemical activation and used for the removal of Blue 49. The adsorption was found to be strongly dependent on pH. The uptake of Blue 49 by

activated carbon was maximal at pH 2. The optimum adsorbent dosage can be used as 0.4 g/100 mL because of the Blue 49 removal efficiency is negligible value at different adsorbent dosage. The adsorption process could be described by pseudo-second-order kinetic models. The thermodynamic studies indicated that was physical adsorption and the data may be useful for environmental technologist in designing treatment plants for Blue 49 removal from wastewaters. The thermodynamic parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$ indicated a spontaneous and endothermic adsorption. According to these results, prepared activated carbon could be used as a low-cost adsorbent to compare with the commercial activated carbon for the removal Blue 49 from wastewater.

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